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PHOTOGRAPHIC SILVER HALIDE EMULSIONS,  
PREPARATIONS, ADDENDA, SYSTEMS AND PROCESSING

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5,314,799, to the abrupt additions of iodide solution at various stages of the precipitation; as illustrated by Reslav et al., *Journal Nauchnoye i Prikladnoye Fotografii i Kinematografi*, Vol. 17, No. 3 (1972) p. 217, Japanese Patent Application 53/66,218 and by Yoshida et al. EPO 0 243 099. Iodide release from an organic compound is illustrated by Takada et al. U.S. Patent 5,389,500 and Kikuchi et al. EPO 0 561 415.

(6) Non-uniform distributions of halides other than iodide are illustrated by Beckett et al. U.S. Patent 3,505,068, Wey et al. U.S. Patent 4,414,306, Klötzer et al. U.S. Patents 4,590,155 and 4,605,610, Ogawa U.S. Patent 5,011,768, Ihama et al. U.S. Patent 5,059,517, Waki et al. U.S. Patent 5,124,244, Sato et al. U.S. Patent 5,155,017, Klein et al. U.K. Patent 1,027,146, Sidwell et al. WO 93/05442, Urabe EPO 0 355 535 and Kawai EPO 0 531 799.

(7) Composite grains can be formed by the epitaxial precipitation of one or more silver salts on a host grain of a differing composition at selected surface sites, as illustrated by Maskasky U.S. Patents 4,094,684, 4,435,501, 4,463,087, 4,471,050 and 5,275,930, Ogawa U.S. Patent 4,735,894, Yamashita et al. U.S. Patent 5,011,767, Uchida U.S. Patent 5,426,023, Haugh et al. U.K. Patent 2,038,792, Koitabashi EPO 0 019 917, Ohya et al. EPO 0 323 215, Takada EPO 0 434 012, Chen EPO 0 498 302 and Berry and Skillman, "Surface Structures and Epitaxial Growths on AgBr Microcrystals", *Journal of Applied Physics*, Vol. 35, No. 7, July 1964, pp. 2165-2169.

(8) The composition of the emulsion grains as precipitated can be modified by halide conversion, typically the displacement of a more soluble silver halide by a less soluble salt, as described by Allentoff et al. U.S. Patent 3,477,852, Evans et al. U.S. Patent 3,622,318, Ogawa U.S. Patent 4,791,053, Hasebe U.S. Patent 4,865,962, Kase et al. U.S. Patent 5,061,615, Inoue U.S. Patent 5,187,058 and EPO 0 295 439, Jäkel German DD 273,906. Weyde et al. U.S. Patent 4,413,055 discloses the conversion silver phosphate grains to silver halide. The halide conversion can be limited to specific positions on the silver halide grains—e.g., to the locations of epitaxial deposits, as described by Maskasky U.S. Patent 4,142,900, or to corners or edges of the grains, as illustrated by Hasebe et al. EPO 0 273 429 and '430 and Yamada et al. German OLS 3,819,241. Tabular grains that exhibit limited edge halide conversion are disclosed by Suga et al. U.S. Patent 5,418,124 and Fenton et al. U.S. Patent 5,476,760.

## B. Grain morphology

(1) The emulsions can be either non-tabular grain or tabular grain emulsions, where tabular grains are those with two parallel major faces each clearly larger than any remaining grain face and tabular grain emulsions are those in which the tabular grains account for at least 30 percent, more typically at least 50 percent, preferably >70 percent and optimally >90 percent of

total grain projected area. The tabular grains can account for substantially all (>97 percent) of total grain projected area. The tabular grain emulsions can be high aspect ratio tabular grain emulsions—i.e.,  $ECD/t > 8$ , where ECD is the diameter of a circle having an area equal to grain projected area and  $t$  is tabular grain thickness; intermediate aspect ratio tabular grain emulsions—i.e.,  $ECD/t = 5$  to 8; or low aspect ratio tabular grain emulsions—i.e.,  $ECD/t = 2$  to 5. The emulsions typically exhibit high tabularity ( $T$ ), where  $T$  (i.e.,  $ECD/t^2$ ) > 25 and ECD and  $t$  are both measured in micrometers ( $\mu m$ ). The tabular grains can be of any thickness compatible with achieving an aim average aspect ratio and/or average tabularity of the tabular grain emulsion. Preferably the tabular grains satisfying projected area requirements are those having thicknesses of <0.3  $\mu m$ , thin (<0.2  $\mu m$ ) tabular grains being specifically preferred and ultrathin (<0.07  $\mu m$ ) tabular grains being contemplated for maximum tabular grain performance enhancements. When the native blue absorption of iodohalide tabular grains is relied upon for blue speed, thicker tabular grains, typically up to 0.5  $\mu m$  in thickness, are contemplated. Choosing particular tabular grain thicknesses to control reflectance and transmission and thereby modify photographic performance characteristics, such as speed and sharpness, are illustrated by Buitano et al. U.S. Patent 5,275,929, Merrill et al. U.S. Patent 5,302,499, and Research Disclosure, Vol. 253, May 1985, Item 25330.

(2) High iodide tabular grain emulsions are illustrated by House U.S. Patent 4,490,458, Maskasky U.S. Patent 4,459,353 and Yagi et al. EPO 0 410 410.

(3) Tabular grains formed of silver halide(s) that form a face centered cubic (rock salt type) crystal lattice structure can have either (100) or (111) major faces. Emulsions containing (111) major face tabular grains, including those with controlled grain dispersities, halide distributions, twin plane spacing, edge structures and grain dislocations as well as adsorbed (111) grain face stabilizers, are illustrated by Wey U.S. Patent 4,399,215, Maskasky U.S. Patents 4,400,463, 4,684,607, 4,713,320, 4,713,323, 5,061,617, 5,176,992, 5,178,997, 5,178,998, 5,183,732, 5,185,239, 5,217,858, 5,221,602, 5,298,387, 5,298,388, 5,389,509, 5,399,478, 5,411,851, 5,411,852, 5,411,853 and 5,418,125, Wey et al. U.S. Patent 4,414,306, Daubendiek et al. U.S. Patents 4,414,310, 4,672,027, 4,693,964 and 4,914,014, Abbott et al. U.S. Patent 4,425,426, Solberg et al. U.S. Patent 4,433,048, Wilgus et al. U.S. Patent 4,434,226, Kofron et al. U.S. Patent 4,439,520, Sugimoto et al. U.S. Patent 4,665,012, Yagi et al. U.S. Patent 4,686,176, Hayashi U.S. Patent 4,748,106, Goda U.S. Patent 4,775,617, Takada et al. U.S. Patent 4,783,398, Saitou et al. U.S. Patents 4,797,354 and 4,977,074, Tufano U.S. Patent 4,801,523, Tufano et al. U.S. Patent 4,804,621, Ikeda et al. U.S. Patent 4,806,461 and EPO 0 485 946, Bando U.S. Patent 4,839,268,

Makino et al. U.S. Patent 4,853,322, Nishikawa et al. U.S. Patent 4,952,491, Houle et al. U.S. Patent 5,035,992, Piggin et al. U.S. Patents 5,061,609 and 5,061,616, Takehara et al. U.S. Patent 5,068,173, Nakamura et al. U.S. Patent 5,096,806, Bell et al. U.S. Patent 5,132,203, Tsaor et al. U.S. Patents 5,147,771, '772, '773, 5,171,659, 5,210,013 and 5,252,453, Jones et al. U.S. Patent 5,176,991, Black et al. U.S. Patent 5,219,720, Maruyama et al. U.S. Patent 5,238,796, Antoniadis et al. U.S. Patent 5,250,403, Delton U.S. Patents 5,372,927 and 5,460,934, Zola et al. EPO 0 362 699, Urabe EPO 0 460 656, Verbeeck EPO 0 481 133, 0 503 700, 0 532 801 and 0 578,772, Jagannathan et al. EPO 0 515 894, Sekiya et al. EPO 0 547 912 and 0 591 883, Kondo EPO 0 600 753, Okutsu EPO 0 610 796, Yamashita et al. EPO 0 611 118 and 0 615 157, Haga EPO 0 616 251, and Kashiwagi et al. EPO 0 634 690. Emulsions containing (100) major face tabular grains are illustrated by Bogg U.S. Patent 4,063,951, Mignot U.S. Patent 4,386,156, Maskasky U.S. Patents 5,264,337, 5,275,930, 5,292,632 and 5,399,477, Brust et al. U.S. Patent 5,314,798, House et al. U.S. Patent 5,320,938 and WO 94/22051, Szajewski et al. U.S. Patent 5,356,764, Chang et al. U.S. Patent 5,413,904, Budz et al. U.S. Patent 5,451,490, Saitou et al. EPO 0 569 971 and Saito et al. Japanese Patent Application 92/77261 and EPO 0 584 644 and 0 645 670, and Brennecke EPO 0 653 669. Ultrathin tabular grains with epitaxy are disclosed by Daubendiek et al. U.S. Patents 5,494,789 and 5,503,971. "Tabular grains with edge faces that clearly lie in different crystal planes the major faces are disclosed by Delton U.S. Patent 5,310,644 and Saitou EPO 0 569 971.

(4) Non-tabular grain emulsions can include grains of any one or combination of a variety of grain shapes, including tabular grains accounting for a minor percentage of total grain projected area. Emulsions prepared by single-jet precipitations, illustrated by Trivelli and Smith, *The Photographic Journal*, Vol. LXXIX, May 1939, pp. 330-338, and Vol. LXXX, July 1940, pp. 285-288, typically produce a wide range of grain shapes. Non-tabular grains can be either regular or irregular--that is, containing one or more twin planes or screw dislocations. Multiply twinned grains of irregular shape, illustrated by Illingsworth U.S. Patent 3,320,069, represent a preferred form of non-tabular grain emulsions. Solvent action typically rounds grain edges to some extent and can produce controlled rounding as illustrated by Koitabashi et al. EPO 0 096 727. Precipitation in high solvent environments (e.g., ammoniacal precipitations illustrated by Duffin *Photographic Emulsion Chemistry*, Focal Press, N.Y. 1966, pp. 60-64, and Glafkides *Photographic Chemistry*, Vol. 1, Fountain Press, London, 1958, pp. 301-304) can produce spherical grain emulsions. Regular grains formed by face centered cubic (rock salt type) crystal lattice structures are typically cubic, octahedral or rhombic dodecahedral grains bounded by crystal faces that lie in (100), (111) or (110) crystal planes,

respectively, although four other, higher index crystal plane families are also possible. Seven regular grain shapes can be produced by selecting all grain facets to lie in the same plane, as illustrated by Maskasky U.S. Patent 4,643,966. Grains bounded by combinations of crystal planes, particularly combinations (100) and (111) crystal planes--e.g., tetradecahedral grains, are highly useful. The variety of regular grain shapes formed by selections or combinations of crystal planes are illustrated by Nishiyama U.S. Patent 4,683,192, Ohya et al. U.S. Patent 4,758,504, Matsuzaka et al. U.S. Patents 4,775,615 and 5,106,725, Ogawa U.S. Patent 4,818,674, Hasebe et al. U.S. Patent 4,820,624, Takada et al. U.S. Patent 4,952,490, Kumashiro et al. U.S. Patent 5,002,865, Schmidt et al. U.S. Patent 5,120,638, Uchida U.S. Patent 5,405,738, Saitou U.S. Patent 5,420,005, Haugh et al. U.K. Patent 2,038,792, Mifune et al. German OLS 4,137,501 and EPO 0 302 528. Non-tabular grains with crystal irregularities, such as dislocations or one or more twin planes, are illustrated by Ogawa U.S. Patent 5,258,272, Takehara U.S. Patent 5,266,450 and Haga et al. EPO 0 645 671. Non-tabular grains can also take hollow, tubular, annular, clam-shell or rod-like shapes, as illustrated by Maskasky U.S. Patents 4,713,320 and 5,385,818, Irving U.S. Patent 4,916,052, Ogawa U.S. Patent 4,946,772, Chang U.S. Patent 5,244,783, Chang et al. U.S. Patents 5,250,408 and 5,298,385, and Martin EPO 0 650 084. Grains with protrusions at the corners of the same halide composition are disclosed by Wen U.S. Patent 5,468,601 and Maskasky U.S. Patent 5,399,477.

(5) The crystal faces of the grains can be modified by the inclusion of declivities or protrusions. Tabular grains with protrusions are illustrated by Maskasky U.S. Patent 4,643,966 and Kishida et al. U.S. Patent 4,814,264. Tabular grains with etched indentations are illustrated by Schmidt U.S. Patent 4,973,547. Non-tabular grains with protrusions are illustrated by Kishida et al. U.S. Patent 4,888,272, Ogawa U.S. Patent 4,895,794, Ohya EPO 0 367 248 and EPO 0 462 581. Non-tabular grains with declivities are illustrated by Iguchi et al. U.S. Patent 4,710,455, Suda et al. U.S. Patent 4,769,315, Amicucci U.S. Patent 4,952,489 and EPO 0 523 464, Urabe U.S. Patent 5,045,443, Okusa EPO 0 410 383 and Koitabashi et al. WO 83/02173.

#### C. Precipitation procedures

The reactants can be added to the reaction vessel in the form of solutions of silver and halide salts, or in the form of preformed silver halide nuclei or fine grains, as described by Mignot U.S. Patent 4,334,012, Saito U.S. Patent 4,301,241, Solberg et al. U.S. Patent 4,433,048, Yamaya U.S. Patent 5,441,864, and Maternaghan U.S. Patent 4,150,994. The individual reactants can be added through surface or subsurface delivery tubes by gravity feed or by delivery apparatus for maintaining control of the rate of delivery and the pH and/or pAg of the reaction vessel contents, as illustrated by Culhane et al. U.S. Patent 3,821,002, Oliver U.S. Patent 3,031,304, and Claes et al.



Photographische Korrespondenz, 102 Band, No. 10, 1967, p. 162.

To obtain rapid distribution of the reactants within the reaction vessel, specially constructed mixing devices can be employed as illustrated by Audran U.S. Patent 2,996,287, McCrossen et al U.S. Patent 3,342,605, Frame et al U.S. Patent 3,415,650, Porter et al U.S. Patent 3,785,777, Saito et al German OLS 2,556,885 and 2,555,364. An enclosed reaction vessel can be employed to receive and mix reactants upstream of the main reaction vessel as illustrated by Forster et al U.S. Patent 3,897,935 and Posse et al U.S. Patent 3,790,386. Formation of silver halide grain nuclei by reacting silver and halide salts in solution can be continued during grain growth, or nucleation and grain growth may be carried out as separate steps in either the same reaction vessel or separate reaction vessels, as described by Posse et al U.S. Patent 3,790,386, Saito U.S. Patent 4,242,445 and Mignot U.S. Patent 4,334,012. Nucleation and growth in two or more separate vessels is illustrated by Urabe U.S. Patent 4,879,208, Ichikawa et al U.S. Patent 5,104,785, Chronis et al U.S. Patent 5,104,786, Urabe et al U.S. Patent 5,196,300, Saitou U.S. Patents 5,202,226, 5,223,388 and 5,238,805, Ichikawa et al U.S. Patent 5,213,772, Goan U.S. Patent 5,378,600, EPO 0 370 116, EPO 0 408 752, German OLS 4,105,649, WO 92/21061, and EPO 0 576 920. The volume of the emulsion in the reaction vessel can be allowed to increase as the reactants are added, or can be controlled by such methods as continuous removal of the emulsion as described in U.K. Patent 1,302,405 and by Terwilliger et al U.S. Patent 4,046,576 or separation of a portion of the dispersing medium as described by Mignot U.S. Patent 4,334,012. Farling et al U.S. Patent 5,083,872, Munch U.S. Patents 5,164,092 and 5,248,418, Vacca U.S. Patent 5,169,750 and WO 92/06765. The reactant solutions or dispersions can be added at a constant rate, or their rate of addition or concentration can be varied continuously or stepwise as described by Hirata et al Bulletin of the Society of Scientific Photography of Japan, No. 16, 1969, p. 1, Irie et al U.S. Patent 3,650,757, Wilgus German OLS 2,107,118 and Saito U.S. Patents 4,242,445 and 4,301,241. The water used in emulsion formation may be subjected to an electrical charge to reduce the silver halide particle size, illustrated by Bragger WO 93/04441.

(2) The monitoring of variables controlling emulsion formation is described in Saito EPO 0 174 021, Chang U.S. Patent 4,933,870, Ichikawa et al U.S. Patents 5,035,991, 5,145,768 and 5,166,015, Jerome U.S. Patent 5,248,577, EPO 0 174 021, EPO 0 577 886 East German DD 288 256, and DD 297 021, and Antoniadis U.S. Patent 5,350,652. The use of a silver electrode for monitoring emulsion precipitation is disclosed in Lin et al U.S. Patent 5,317,521.

(3) Mixing apparatus directed to the manufacture of silver halide emulsions is illustrated by Saito U.S. Patent 5,096,690, EPO 0 474 221, EPO 0 493 625 and EPO 0 523 842.

## D. Grain modifying conditions and adjustments

(1) Emulsion precipitation is conducted in the presence of silver ions, halide ions and an aqueous dispersing medium including, at least during grain growth, a peptizer. Grain structure and properties can be selected by control of precipitation temperatures, pH and the relative proportions of silver and halides ions in the dispersing medium. To avoid fog, precipitation is customarily conducted on the halide side of the equivalence point (the point at which silver and halide ion activities are equal). Manipulations of these basic parameters are illustrated by the citations including emulsion precipitation descriptions and are further illustrated by Matsuzaka et al U.S. Patent 4,497,895, Yagi et al U.S. Patent 4,728,603, Sugimoto U.S. Patent 4,755,456, Kishita et al U.S. Patent 4,847,190, Joly et al U.S. Patent 5,017,468, Wu U.S. Patent 5,166,045, Weberg et al U.S. Patent 5,318,888, Goan U.S. Patent 5,420,007, Loiacono et al U.S. Patent 5,437,971, Shibayama et al EPO 0 328 042, Kawai EPO 0 531 799, Okutsu et al EPO 0 610 597, Van den Zegel EPO 0 569 075, Kashi EPO 0 613 042, Vacca et al EPO 0 645 672, Verbeeck EPO 0 649 051, 0 651 284 and 0 682 287, Saito EPO 0 670 515, and Research Disclosure, Vol. 375, July 1995, Item 37542.

(2) Reducing agents present in the dispersing medium during precipitation can be employed to increase the sensitivity of the grains, as illustrated by Takada et al U.S. Patent 5,061,614, Takada U.S. Patent 5,079,138 and EPO 0 434 012, Inoue U.S. Patent 5,185,241, Predy et al 5,389,510, Yamashita et al EPO 0 369 491, Ohashi et al EPO 0 371 338, Katsumi EPO 0 435 270 and 0 435 355 and Shibayama EPO 0 438 791. Chemically sensitized core grains can serve as hosts for the precipitation of shells, as illustrated by Porter et al U.S. Patents 3,206,313 and 3,317,322, Evans U.S. Patent 3,761,276, Atwell et al U.S. Patent 4,035,185, Evans et al U.S. Patent 4,504,570, and Fujita et al U.S. Patent 5,424,168.

(3) Dopants (any grain occlusions other than silver and halide ions) can be employed to modify grain structure and properties. Periods 3-7 ions, including Group VIII metal ions (Fe, Co, Ni and the platinum metals (pm) Ru, Rh, Pd, Re, Os, Ir and Pt), Mg, Al, Ca, Sc, Ti, V, Cr, Mn, Cu, Zn, Ga, As, Se, Sr, Y, Mo, Zr, Nb, Cd, In, Sn, Sb, Te, Ba, La, W, Au, Hg, Tl, Pb, Bi, Ce and U, can be introduced during precipitation. The dopants can be employed (a) to increase the sensitivity of either (a1) direct positive or (a2) negative working emulsions, (b) to reduce (b1) high or (b2) low intensity reciprocity failure, (c) to (c1) increase, (c2) decrease or (c3) reduce the variation of contrast, (d) to reduce pressure sensitivity, (e) to decrease dye desensitization, (f) to increase stability, (g) to reduce minimum density, (h) to increase maximum density, (i) to improve room light handling and (j) to enhance latent image formation in

response to shorter wavelength (e.g., X-ray or gamma radiation) exposures. For some uses any polyvalent metal ion (pvmi) is effective. The selection of the host grain and the dopant, including its concentration and, for some uses, its location within the host grain and/or its valence, can be varied to achieve aim photographic properties, as illustrated by B. H. Carroll, "Iridium Sensitization: A Literature Review", *Photographic Science and Engineering*, Vol. 24, No. 6, Nov./Dec. 1980, pp. 265-267, Hochstetter U.S. Patent 1,951,933, De Witt U.S. Patent 2,628,167, Mueller et al U.S. Patent 2,950,972, Spence et al U.S. Patent 3,687,676, Gilman et al U.S. Patent 3,761,267, Ohkubo et al U.S. Patent 3,890,154, Iwao et al U.S. Patent 3,901,711, Yamasue et al U.S. Patent 3,901,713, Habu et al U.S. Patent 4,173,483, Atwell U.S. Patent 4,269,927, Weyde U.S. Patent 4,413,055, Akimura et al U.S. Patent 4,452,882, Menjo et al U.S. Patent 4,477,561, Habu et al U.S. Patent 4,581,327, Kobuta et al U.S. Patent 4,643,965, Yamashita et al U.S. Patent 4,806,462, Grzeskowiak et al U.S. Patent 4,828,962, Janusonis U.S. Patent 4,902,611, Inoue et al U.S. Patent 4,981,780, Kim U.S. Patent 4,997,751, Kuno U.S. Patent 5,051,344, Shiba et al U.S. Patent 5,057,402, Maekawa et al U.S. Patent 5,134,060, Kawai et al U.S. Patent 5,153,110, Johnson et al U.S. Patent 5,164,292, Asami U.S. Patents 5,166,044 and 5,204,234, Wu U.S. Patent 5,166,045, Yoshida et al 5,229,263, Marchetti et al U.S. Patents 5,264,336 and 5,268,264, MacIntyre U.S. Patent 5,252,451, Bell U.S. Patents 5,256,530, 5,500,335, 5,474,888 and 5,480,771, Asami U.S. Patent 5,278,872, Murakami et al U.S. Patent 5,382,503, Ohm et al U.S. Patent 5,503,970, Komorita et al EPO 0 244 184, Ohsima et al EPO 0 312 999, Miyoshi et al EPO 0 488 737 and EPO 0 488 601, Ihama et al EPO 0 368 304, Tashiro EPO 0 405 938 and EPO 0 563 946, Suzuki et al EPO 0 556 715, Hoshina EPO 0 603 654, Nakayama et al EPO 0 687 948, Mifune EPO 0 619 515, Budz WO 93/02390, and Research Disclosure, Vol. 367, Nov. 1994, Item 36736. Dividing emulsions with different doping levels into separate emulsion layers is disclosed by Fujiwara et al U.S. Patent 5,368,994.

(4) When dopant metals are present during precipitation in the form of coordination complexes, particularly tetra- and hexa-coordination complexes, both the metal ion and the coordination ligands can be occluded within the grains. Coordination ligands, such as halo, aquo, cyano, cyanate, fulminate, thiocyanate, selenocyanate, tellurocyanate, nitrosyl, thionitrosyl, azide, oxo, carbonyl and ethylenediamine tetraacetic acid (EDTA) ligands have been disclosed and, in some instances, observed to modify emulsion properties, as illustrated by Grzeskowiak U.S. Patent 4,847,191, McDugle et al U.S. Patents 4,933,272, 4,981,781 and 5,037,732, Marchetti et al U.S. Patent 4,937,180, Keever et al U.S. Patent 4,945,035, Hayashi U.S. Patent 5,112,732, Goto U.S. Patent 5,283,169, Murakami et al EPO 0 509 674, Ohya et al EPO 0 513 748, Brennecke EPO 0 647 877, Janusonis WO 91/10166,

Beavers WO 92/16876, Pietsch et al German DD 298,320. Metal coordination complexes containing organic ligands that function as dopants are illustrated by Bigelow U.S. Patent 4,092,171 and Olm et al 5,360,712.

(5) Oligomeric coordination complexes can also be employed to modify grain properties, as illustrated by Evans et al U.S. Patent 5,024,931.

(6) Emulsion addenda that adsorb to grain surfaces, such as antifogants, stabilizers and dyes, can also be added to the emulsions during grain precipitation. Precipitation in the presence of spectral sensitizing dyes is illustrated by Locker U.S. Patent 4,183,756, Locker et al U.S. Patent 4,225,666, Ihama et al U.S. Patents 4,683,193 and 4,828,972, Takagi et al U.S. Patent 4,912,017, Ishiguro et al U.S. Patent 4,983,508, Nakayama et al U.S. Patent 4,996,140, Steiger U.S. Patent 5,077,190, Brugger et al U.S. Patent 5,141,845, Metoki et al U.S. Patent 5,153,116, Asami et al EPO 0 287 100 and Tadaaki et al EPO 0 301 508. Non-dye addenda are illustrated by Klötzer et al U.S. Patent 4,705,747, Ogi et al U.S. Patent 4,868,102, Ohya et al U.S. Patent 5,015,563, Bahnmüller et al U.S. Patent 5,045,444, Maeka et al U.S. Patent 5,070,008 and Vandenabeele et al EPO 0 392 092.

#### E. Blends, layers and performance categories

(1) The emulsions can be either monodispersed or polydispersed as precipitated. To improve photographic efficiency it is generally preferred to minimize the dispersity of each coprecipitated grain population and to subsequently blend emulsions, if necessary, to match aim performance characteristics.

(2) The size-frequency distributions of emulsion grains can be narrowed by physical separation techniques, as illustrated by Audran et al U.S. Patent 3,326,641 and/or, more conveniently, by controlled ripening during and immediately following precipitation, as illustrated by Research Disclosure, Vol. 232, Aug. 1983, Item 23212. The use of ammonia as a ripening agent during precipitation is illustrated by Duffin Photographic Emulsion Chemistry, Focal Press, N.Y. 1966, pp. 60-64, Glafkides Photographic Chemistry, Vol. 1, Fountain Press, London, 1958, pp. 301-304, Maternaghan U.S. Patents 4,184,877 and '878, Wey U.S. Patent 4,399,215 and Wilhite et al U.S. Patent 4,678,744. Excess halide ion ripened emulsions are illustrated by Duffin, cited above, pp. 60-72. Amine ripened emulsions are ripened emulsions are illustrated by Heki et al U.S. Patent 4,469,784. Among preferred emulsions are those prepared using ripening agents that contain sulfur, as illustrated by the anionic sulfur-substituted triazolum inner salt ripened emulsions of Mifune et al U.S. Patent 4,631,253, the thiocyanate ripened emulsions illustrated by Illingsworth U.S. Patent 3,320,069 and Koitabashi et al U.S. Patent 4,514,491, the

thioether ripened emulsions illustrated by McBride U.S. Patent 3,271,157, Mikawa U.S. Patent 4,198,240, Bryan et al U.S. Patents 4,695,534, 535 and 4,713,822, Herz et al U.S. Patent 4,782,013 and Friour et al U.S. Patent 4,865,965 and the benzenesulfinate ripened emulsions of Jakeli et al East German Patents DD 294,576 and DD 296,810. Oxidizing agents can be employed to arrest the ripening action of sulfur-containing ripening agents, as illustrated by Mifune et al U.S. Patents 4,665,017 and 4,681,838, Yamada et al U.S. Patent 4,678,745, Murai et al U.S. Patent 4,863,845 and Iwasaki et al U.S. Patent 5,030,552. Mifune et al U.S. Patent 4,801,524 discloses the use of an oxidizing agent to arrest the action of a sulfur-containing growth inhibitor. Emulsions ripened using weak silver halide solvents, such as ammonia salts, are illustrated by Perignon U.S. Patent 3,784,381 and Research Disclosure, Vol. 134, June 1975, Item 13452. Ripening not only reduces grain dispersity, but can also redistribute halides to produce uniform halide compositions, as illustrated by the citations above showing uniform intra-grain iodide. The interruption of salt addition for a ripening interval following grain nucleation to reduce dispersity is particularly preferred in preparing tabular grain emulsions, as illustrated by Himmelwright U.S. Patent 4,477,565, Nottorf U.S. Patent 4,722,886, Ellis U.S. Patent 4,801,522, Saitou U.S. Patent 4,945,037, Grzeskowiak U.S. Patent 5,028,521, Buntaine et al U.S. Patent 5,013,641, Antoniadis et al U.S. Patent 5,250,403, Tsaur et al U.S. Patent 5,210,013 and 5,252,453, House et al U.S. Patent 5,320,938, but more generally useful, as illustrated by Yamamoto et al U.S. Patent 5,204,235. Tabular grain emulsions can be produced by the extended ripening of non-tabular grain emulsions, as illustrated by Mignot U.S. Patent 4,386,156 and French Patent 2,534,036 and Lothar German OLS 3,739,470. Whereas the dispersity of grains is generally measured in terms of the coefficient of variation (COV) of equivalent circular diameter (ECD), the dispersities of the diameters and thicknesses of tabular grains can be independently addressed, as illustrated by Sutton et al U.S. Patent 5,300,413 and Matsuzaka EPO 0 515 106.

(3) The silver and halide ions introduced during grain growth can be supplied as dissolved salts or as fine grains, typically as a Lippmann emulsion. Iodide addition in fine grains and/or as soluble salts is illustrated by Piggin et al U.S. Patents 5,061,609 and 5,061,616, Yamada et al U.S. Patent 5,206,134, Wada et al EPO 0 391 356, Ohtani EPO 0 462 528 and Wharton EPO 0 477 772. Ripening one grain population onto another is illustrated by Lapp et al U.S. Patent 4,379,837. Core-shell grains can be formed by blending monodispersed finer and coarser grain emulsions, followed by ripening out the finer grains as shells on the coarser grains, as illustrated by Porter et al U.S. Patents 3,206,313 and 3,317,322. Grains that remain a permanent part of the emulsion can be introduced during precipitation. Wey et al U.S. Patent 4,552,838 illustrates varied host

grain introductions during precipitation to achieve varied grain size-frequency distributions.

(4) The emulsions can be surface-sensitive emulsions--i.e., emulsions that form latent images primarily on the surfaces of the silver halide grains (as typically occurs absent intentional grain modification) including those that form latent images at selected surface sites, as illustrated by Kofron et al U.S. Patent 4,439,520, Maskasky U.S. Patent 4,435,501, Yamada et al U.S. Patent 4,968,595 and Hasebe et al U.S. Patent 4,820,624 or internal latent image-forming emulsions--i.e., emulsions that form latent images predominantly in the interior of the silver halide grains (typically achieved by internal crystal irregularities, dopant incorporation or chemical sensitization of core surfaces), as illustrated by Knott et al U.S. Patent 2,456,953, Davey et al U.S. Patent 2,592,250, Porter et al U.S. Patents 3,206,313 and 3,327,322, Berriman U.S. Patent 3,367,778, Bacon et al U.S. Patent 3,447,927, Evans 3,761,276, Morgan U.S. Patent 3,917,483, Gilman et al U.S. Patent 3,979,213, Miller U.S. Patent 3,767,413, Arai U.S. Patent 5,043,259, Nagaoka et al U.S. Patent 5,156,946 and EPO 0 272 675, Harvey et al U.K. 2,222,694 and EPO 0 445 444.

(5) The emulsions that contain unfogged surface or internal latent image forming grains can produce negative images or, by using reversal processing, can produce positive images. Direct positive images can be produced by using emulsions that contain unfogged internal latent image-forming grains in combination with fogging development, as illustrated by Ives U.S. Patent 2,563,785, Evans U.S. Patent 3,761,276, Atwell et al 4,035,185, Evans et al U.S. Patent 4,504,570, Kriebel U.S. Patent 4,704,349 and EPO 0 340 168, Ogi et al U.S. Patent 4,868,102, Tosaka et al U.S. Patent 4,917,991, Inoue et al U.S. Patent 4,996,137, Tanemura et al U.S. Patent 5,081,009 and EPO 0 381 160, Shuto et al U.S. Patent 5,104,784, Pugh et al WO 91/12566 and Research Disclosure, Vol. 151, Nov. 1976, Item 15162, or by using emulsions that contain surface-fogged grains, as illustrated by Illingsworth U.S. Patents 3,501,305, '306 and '307, Berriman U.S. Patent 3,367,778, Research Disclosure, Vol. 134, June 1975, Item 13452, Kurz U.S. Patent 3,672,900, Judd et al U.S. Patent 3,600,180, Taber et al U.S. Patent 3,647,463, Hine U.S. Patent 4,814,263, Kishita et al U.S. Patent 4,847,190, Besio U.S. Patent 4,849,326, Arai U.S. Patent 5,043,259, Mitsuhashi U.S. Patent 5,206,132, Kazuhiro EPO 0 146 302 and Graindourze EPO 0 477 436.

(6) Aim characteristics are routinely achieved by blending separately precipitated emulsions. Similar emulsions differing in grain size, shape or dispersity can be blended to achieve aim size-frequency grain distributions. Particular blend selections are illustrated by Bando U.S. Patent 4,727,016, Asami et al U.S. Patent 4,745,047, Kuramoto et al U.S. Patent 4,939,078, Yoshizawa et al U.S. Patent 4,943,518, Mitsubishi U.S. Patent 5,206,132, Momoki et al U.S. Patent 4,803,152, Okumura et

al SIR H1450, and Friour et al EPO 0 618 485. Dissimilar emulsions can be blended to achieve varied photographic effects. Kofron et al U.S. Patent 4,439,520 discloses reduced granularity to result from blending silver chloride grains with tabular grains. Kim U.S. Patent 5,176,990 discloses increased speed by blending a finer grain silver salt with silver iodohalide grains, preferably tabular grains. Ohya et al U.S. Patent 5,039,601 discloses extending exposure latitude by blending in desensitizing metal ion doped grains. Giannesi U.S. Patent 4,812,390 discloses blending coarser light sensitive grains with light insensitive grains having a spectral sensitizing dye adsorbed. Blends of surface-sensitive silver iodohalide emulsions and surface fogged emulsions can be employed in reversal processed photographic elements, as illustrated by Groet U.S. Patent 4,082,553, and in negative imaging, as illustrated by Groet et al U.S. Patent 4,201,841. Newmiller U.S. Patent 4,865,964 discloses reduced granularity to result from blending high and low aspect ratio silver (iodo)bromide grains. Dickerson U.S. Patent 4,520,098 discloses blending high iodide grains with spectrally sensitized tabular grains to reduce dye stain. Dickerson U.S. Patent 5,391,469 blends silver bromide tabular grains with and without incorporated iodide to reduce presensitization. Tabular grain emulsions in reversal processed photographic elements can be blended with smaller grains to improve image properties, as illustrated by Sowinski et al U.S. Patent 4,656,122. Kim et al U.S. Patent 5,236,817. Droin et al U.S. Patent 5,378,591. Chen et al U.S. Patent 5,389,507, and Cohen et al U.S. Patent 5,391,468. Takada et al EPO 0 369 486 teaching blending fine high chloride grains to act as a carrier for adsorbed components capable of forming during processing salts less soluble than silver bromide. Maekawa et al EPO 0 488 601 discloses blending dissimilarly doped emulsions to increase exposure latitude and invariance of response. Direct positive silver images produced by fogging development can exhibit increased covering power by fogging smaller internal latent image-forming or internally fogged grains, as illustrated by Silverman et al Re. 32,097 and 32,149, and can exhibit greater processing stability by blending desensitized grains, as illustrated by Ogi et al U.S. Patent 4,910,130. Direct positive, emulsion blends of internal latent image forming grains with finer grains with (100) crystal plane faces are illustrated by Grünecker et al German OLS 3,644,223. Blends of silver iodohalide surface sensitive emulsions and internally fogged grains can be employed to increase speed, as illustrated by Luckey et al U.S. Patents 2,996,382 and 3,397,987, Luckey U.S. Patent 3,695,881, Research Disclosure, Vol. 134, June 1975, Item 13452, and Kurz Research Disclosure, Vol. 122, June 1974, Item 12233.

(7) Instead of blending latent image forming silver halide grains responsive to the same region of the spectrum in the same emulsion layer, they can be coated in two, three or more

emulsion layers, as illustrated by Zeilman and Levi Making and Coating Photographic Emulsions, Focal Press, 1964, pp. 236-238, Wyckoff U.S. Patents 3,663,228 and 3,849,138, Kumai et al U.S. Patent 3,843,369, Ranz et al U.S. Patent 4,173,479, Kato et al U.S. Patent 4,145,219, Lohmann et al U.S. Patent 4,186,011, Hamada U.S. Patents 4,438,194 and 4,414,308, Watanabe et al U.S. Patent 4,564,587, Mochizuki et al U.S. Patent 4,639,410, Sauerfing et al U.S. Patent 4,788,133, Ikeda et al U.S. Patent 4,818,410, Suga U.S. Patent 5,057,409, Yagushi et al U.S. Patent 5,091,293, Shibahara et al U.S. Patent 5,268,262, Ohmatsu et al U.S. Patent 5,310,636, Endres EPO 0 413 204, Bockley et al U.S. Patent 1,121,470 and U.K. Patent 923,045. Using faster and slower emulsions longer exposure latitudes and higher speeds with equivalent granularities can be realized when the emulsions are coated in separate layers with the faster emulsion positioned to receive light prior to the slower emulsion, as compared to blending the emulsions. Chang et al U.S. Patents 5,314,793 and 5,360,703 combine this feature with iodide management further increases in speed. When a slower emulsion layer is coated over a faster emulsion, increased contrast is obtained. A light insensitive emulsion can be coated over an imaging emulsion layer to impart room light handling, as illustrated by Gingello et al WO 91/12562 or to increase developability, as illustrated by Bell et al U.S. Patent 5,354,649. Employing a silver chloride emulsion layer to improve sharpness is disclosed by Brennecke U.S. Patent 5,360,704. Underlying emulsion layers are also useful in reducing halation in overlying emulsion layers.

## II. Vehicles, vehicle extenders, vehicle-like addenda and vehicle related addenda

A. Gelatin and hydrophilic colloid peptizers  
(1) Photographic silver halide emulsion layers and other layers on photographic elements can contain various colloids alone or in combination as vehicles. Suitable hydrophilic materials include both naturally occurring substances such as proteins, protein derivatives, cellulose derivatives-e.g., cellulose esters, gelatin-e.g., alkali-treated gelatin (cattle bone or hide gelatin) or acid-treated gelatin (pigskin gelatin), gelatin derivatives-e.g., acetylated gelatin, phthalated gelatin and the like, polysaccharides such as dextran, gum arabic, zein, casein, pectin, collagen derivatives, collodion, agar-agar, arrowroot, albumin and the like as described in Yutzy et al U.S. Patents 2,614,928 and '929, Lowe et al U.S. Patents 2,691,582, 2,614,930, '931, 2,327,808 and 2,448,534, Gates et al U.S. Patents 2,787,545 and 2,956,880, Himmelmann et al U.S. Patent 3,061,436, Farrell et al U.S. Patent 2,816,027, Ryan U.S. Patents 3,132,945, 3,138,461 and 3,186,846, Deusch et al U.K. Patent 1,167,159 and U.S. Patents 2,960,405 and 3,436,220, Geary U.S. Patent 3,486,896, Gazzard U.K. Patent 793,549, Gates et al U.S.

Patents: 2,992,213, 3,157,506, 3,184,312 and 3,539,353, Miller et al U.S. Patent 3,227,571, Boyer et al U.S. Patent 3,532,502, Malan U.S. Patent 3,551,451, Lohmer et al U.S. Patent 3,532,502, Luciani et al U.K. Patent 1,186,790, U.K. Patent 1,489,080 and Hori et al Belgian Patent 856,631, U.K. Patent 1,490,644, U.K. Patent 1,483,551, Arase et al U.K. Patent 1,459,906, Salo U.S. Patents 2,110,491 and 2,311,086, Pallesen U.S. Patent 2,343,650, Yutzy U.S. Patent 2,322,085, Lowe U.S. Patent 2,563,791, Talbot et al U.S. Patent 2,725,293, Hilborn U.S. Patent 2,748,022, DePaauw et al U.S. Patent 2,956,883, Ritchie U.K. Patent 2,095, DeStubner U.S. Patent 1,752,069, Sheppard et al U.S. Patent 2,127,573, Lieng U.S. Patent 2,256,720, Gaspar U.S. Patent 2,361,936, Farmer U.K. Patent 15,727, Stevens U.K. Patent 1,062,116, Yamamoto et al U.S. Patent 3,923,517 Maskasky U.S. Patent 5,284,744, Bagchi et al U.S. Patents 5,318,889 and 5,378,598, and Wrathall et al U.S. Patent 5,412,075.

(2) Relatively recent teachings of gelatin and hydrophilic colloid peptizer modifications and selections are illustrated by Moll et al U.S. Patents 4,990,440 and 4,992,362 and EPO 0 285 994, Koepff et al U.S. Patent 4,992,100, Tanji et al U.S. Patent 5,024,932, Schulz U.S. Patent 5,045,445, Dumas et al U.S. Patent 5,087,694, Nasrallah et al U.S. Patent 5,210,182, Specht et al U.S. Patent 5,219,992, Nishibori U.S. Patent 5,225,536, U.S. Patent 5,244,784, Weatherill U.S. Patent 5,391,477, Lewis et al U.S. Patent 5,441,865, Kok et al U.S. Patent 5,439,791, Tavernier EPO 0 532 094, Kadowaki et al EPO 0 551 994, Michiels et al EPO 0 628 860, Sommerfeld et al East German DD 285 255, Kuhrt et al East German DD 299 608, Wetzel et al East German DD 289 770 and Farkas U.K. Patent 2,231,968.

(3) Where the peptizer is gelatin or a gelatin derivative it can be treated prior to or during emulsion precipitation with a methionine oxidizing agent. Examples of methionine oxidizing agents include NaOCl, chloramine, potassium monopersulfate, hydrogen peroxide and peroxide releasing compounds, ozone, thiosulfates and alkylating agents. Specific illustrations are provided by Maskasky U.S. Patents 4,713,320 and 4,713,323, King et al U.S. Patent 4,942,120, Takada et al EPO 0 434 012 and Okumura et al EPO 0 553 622.

(4) Silica and derivative compounds can be employed as peptizers and protective colloids in photographic emulsions, as illustrated by Vandenabeele (et al) EPO 0 392 092, 0 517 961 and 0 528 476 and Kunio Japanese Patent Application 91-140713.

(5) The photographic elements and particularly the gelatin and gelatin derivative containing layers of the photographic elements can be protected against by biological degradation by the addition of agents for arresting biological activity (biocides and/or biostats), such as illustrated by Kato et al U.S. Patent 4,923,790, Sasaki et al U.S. Patent 4,997,752, Miyata et al U.S. Patent 5,185,240, Noguchi et al U.S. Patent 5,198,329, Wada EPO 0 331 319, Ogawa et al EPO 0 429 240, Meisel East German

DD 281,265, Jäkel et al East German DD 298,460, Hartmann et al East German 299,063 and Cawse U.K. Patent 2,223,859.

## B. Hardeners

(1) The layers of the photographic element containing cross-linkable colloids, particularly the gelatin-containing layers, can be hardened by various organic and inorganic hardeners, such as those described in T. H. James, *The Theory of the Photographic Process*, 4th Ed., MacMillan, 1977, pp. 77-87. The hardeners can be used alone or in combination and in free or in blocked form.

(2) Typical useful hardeners include formaldehyde and free dialdehydes such as succinaldehyde and glutaraldehyde as illustrated by Allen et al U.S. Patent 3,232,764, blocked dialdehydes as illustrated by Kaszuba U.S. Patent 2,586,168, Jeffreys U.S. Patent 2,870,013 and Yamamoto et al U.S. Patent 3,819,608; a-diketones as illustrated by Allen et al U.S. Patent 3,819,608; active esters of the type described by Burness et al U.S. Patent 3,542,558; sulfonate esters as illustrated by Burness et al U.S. Patents 2,725,305 and 2,726,162; active halogen compounds as illustrated by Burness U.S. Patent 3,106,468, Silverman et al U.S. Patent 3,839,042, Ballantine et al U.S. Patent 3,951,940 and Himmelmann et al U.S. Patent 3,174,861 and Vermeersch et al U.S. Patent 4,879,209; s-triazines and diazines as illustrated by Yamamoto et al U.S. Patent 3,325,287, Anderau et al U.S. Patent 3,288,775, Stauner et al U.S. Patent 3,992,366, Terashima et al U.S. Patent 5,102,780 and Komorita et al EPO 0 244 184; epoxides as illustrated by Allen et al U.S. Patent 3,047,394, Burness U.S. Patent 3,189,459, Vermeersch et al U.S. Patent 4,820,613, Komorita 4,837,143, Helling et al EPO 0 301 313 and Birt et al German OLS 1,085,663; aziridines as illustrated by Allen et al U.S. Patent 2,950,197, Burness et al U.S. Patent 3,271,175 and Sato et al U.S. Patent 3,575,705; active olefins having two or more active bonds as illustrated by Burness et al U.S. Patents 3,490,911, 3,539,644 and 3,841,872 (Reissue 29,305), Cohen U.S. Patent 3,640,720, Kleist et al German OLS 872,153, Allen U.S. Patent 2,992,109, Itahasi et al U.S. Patent 4,874,687, Okamura et al U.S. Patent 4,897,344, Ikenoue et al U.S. Patent 5,071,736, Delfino et al U.S. Patent 5,246,824 and Helling et al German OLS 3,724,672; blocked active olefins as illustrated by Burness et al U.S. Patent 3,360,372, Wilson U.S. Patent 3,345,177 and Himmelmann et al U.S. Patents 4,845,0234 and 4,894,324; carbodimides as illustrated by Blout et al German Patent 1,148,446; isoxazolium salts unsubstituted in the 3-position as illustrated by Burness et al U.S. Patent 3,321,313; esters of 2-alkoxy-N-carboxyhydroquinoline as illustrated by Bergthaller et al U.S. Patent 4,013,468; N-carbamoyl pyridinium salts as illustrated by Himmelmann et al U.S. Patents 3,880,665 and 4,063,952, Okamura et al U.S. Patent 4,828,974, Schranz et al U.S. Patent 4,865,940, Roche et al U.S. Patent 4,978,607, Schweicher et al U.S. Patent 4,942,068 and Helling et al EPO 0 370 226; carbamoyl oxypryri-





Patent 4,391,903. Chen U.S. Patent 4,401,787, Karino et al U.S. Patent 4,396,698, Fitzgerald U.S. Patent 4,315,071, Fitzgerald et al U.S. Patent 4,350,759, Helling U.S. Patent 4,513,080, Brück et al U.S. Patent 4,301,240, Campbell et al U.S. Patent 4,207,109, Chuang et al U.S. Patent 4,145,221, Berghallier et al U.S. Patent 4,334,013, Helling U.S. Patent 4,426,438, Anderson et al U.S. Patent 5,366,855, Valentini U.S. Patent 5,374,509, Ruger U.S. Patent 5,407,792, Iwagaki et al EPO 0 131 161, and Bennett et al WO 94/13479 and WO 94/13481.

(2) Recent illustrations of synthetic polymers, especially latex polymers, added to various layers of photographic elements to achieve specific results, such as, to increase viscosity, to reduce curl, to decrease pressure sensitivity, to increase dimensional stability, to prevent color stain, to improve dryability and scratch resistance, to deliver photographically useful materials to prevent wandering of filter dyes, to promote flocculation or coagulation and as binders, are provided by Roth (et al) German DE Patent 4,034,871 and East German DD 295,420, Sasaki et al 4,975,360, Deppen et al U.S. Patent 5,015,566, Kraft et al U.S. Patent 5,070,006, Factor U.S. Patents 5,006,450 and 5,077,187, Ono et al U.S. Patent 4,983,506, Kawai U.S. Patent 4,914,012, Matakaeyama et al U.S. Patent 5,219,718, Fujita et al U.S. Patent 5,374,498, Westfal et al U.S. Patent 5,374,510, Ogawa et al U.S. Patent 5,376,434, Texter et al U.S. Patent 5,441,854, Helling et al U.S. Patent 5,455,154, Hesse et al German OLS 276,743, Motoki et al EPO 0 319 920, Arai (et al) EPO 0 477 670 and EPO 0 510 961 Nair et al EPO 0 552 802, Takamuki EPO 0 587 390, Bagchi et al EPO 0 597 289, Tachibana EPO 0 614 116, and Morita et al EPO 0 615 158.

(3) Recent illustrations of photographic elements including polymeric layers for the purpose of reflecting released development inhibitors, serving as barriers to the diffusion of alkaline processing compositions, to improve adhesion of emulsion layers to the film base, as stress-absorbing layers, as scratch resistant layers, and as alkali-soluble binders for antihalation layers are set forth in Grous U.S. Patent 4,914,011, Shiratsuchi et al U.S. Patent 5,212,051, Lushington et al U.S. Patent 5,300,417, Visconte et al U.S. Patent 5,300,418, Texter et al U.S. Patent 5,370,967, Quintens et al U.S. Patent 5,372,924, Szajewski et al EPO 0 535 535, Cause et al EPO 0 557 785, Lushington et al EPO 0 520 394 and Daems et al EPO 0 462 330.

(4) Recent illustrations of polymeric mordants for use in photographic elements are disclosed in Shibata et al U.S. Patent 4,774,162, Janssens et al U.S. Patent 4,855,211, Toya et al U.S. Patent 5,015,562 and Yamanouchi et al U.S. Patents 5,023,162 and 5,104,778.

### III.

#### Emulsion washing

The silver halide emulsion can be unwashed or washed to remove soluble salts. Ito et al EPO 0 462 543 teaches delaying washing until the emulsion grains are fully formed. The soluble salts can be removed by chill-setting and leaching as illustrated by Craft U.S. Patent 2,316,845 and McFall et al U.S. Patent 3,396,027, by coagulation washing as illustrated by Hewitson et al U.S. Patent 2,618,556, Yutzy et al U.S. Patents 2,614,928 and '929, Yackel U.S. Patent 2,565,418, Hart et al U.S. Patent 3,241,969, Waller U.S. Patent 2,489,341, Klinger U.K. Patent 1,305,409, Dersch et al U.K. Patent 1,167,159 and Goan et al U.S. Patent 4,990,439, by centrifugation and decantation of a coagulated emulsion as illustrated by Murray U.S. Patent 2,463,794, Ujihara et al U.S. Patent 3,707,378, Audran U.S. Patent 2,996,287 and Timson U.S. Patent 3,498,454, by employing hydrocyclohexanes alone or in combination with centrifuges as illustrated by U.K. Patent 1,336,692, Claes U.K. Patent 1,356,573 and Ushomirskii et al, Soviet Chemical Industry, Vol. 6, No. 3, 1974, pp. 181-185, by diafiltration with a semipermeable membrane as illustrated by Research Disclosure, Vol. 102, October, 1972; Item 10208, Hagenmaier et al Research Disclosure, Vol. 131, March, 1975, Item 13122, Bonnet Research Disclosure, Vol. 135, July, 1975, Item 13577, Berg et al German OLS 2,436,461 and Bolton U.S. Patent 2,495,918, or by employing an ion-exchange resin, as illustrated by Maley U.S. Patent 3,782,953 and Noble U.S. Patent 2,827,428. The emulsions, with or without sensitizers, can be dried and stored prior to use as illustrated by Research Disclosure, Vol. 101, September, 1972, Item 10152.

### IV.

#### Chemical sensitization

(1) The silver halide emulsions can be chemically sensitized with active gelatin as illustrated by T.H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, pp. 67-76, or with middle chalcogen (sulfur, selenium or tellurium), gold, a platinum metal (platinum, palladium, rhodium, ruthenium, iridium and osmium), rhodium or phosphorus sensitizers or combinations of these sensitizers, such as at pAg levels of from 5 to 10, pH levels of from 5 to 8 and temperatures of from 30 to 80°C, as illustrated by Research Disclosure, Vol. 120, April, 1974, Item 12008, Research Disclosure, Vol. 134, June, 1975, Item 13452, Sheppard et al U.S. Patent 1,623,499, Matthies et al U.S. Patent 1,673,522, Waller et al U.S. Patent 2,399,083, Smith et al U.S. Patent 2,448,060, Damschroder et al U.S. Patent 2,642,361, McVeigh U.S. Patent 3,297,447, Dunn U.S. Patent 3,297,446, McBride U.K. Patent 1,315,755, Berry et al U.S. Patent 3,772,031, Gilman et al U.S. Patent 3,761,267, Ohi et al U.S. Patent 3,857,711, Klinger et al U.S. Patent 3,565,633, Oftedahl U.S. Patents 3,901,714 and 3,904,415, Ohshima U.S. Patent 5,432,052, Brust et al U.S. Patent 5,411,854, Bell U.S. Patent 5,385,817, Yoshida et al U.S. Patent 5,364,750, Heremans EPO 0 610 609,



Ohzeki EPO 0 580 179, and Simons U.K. Patent 1,396,696, chemical sensitization being optionally conducted in the presence of thiocyanate derivatives as described in Damschroder U.S. Patent 2,642,361, thioether compounds as disclosed in Lowe et al U.S. Patent 2,521,926, Williams et al U.S. Patent 3,021,215 and Bigelow U.S. Patent 4,054,457, Ikeda U.S. Patent 5,370,985, and azaindenes, azapyridazines and azapyrimidines as described in Dostes U.S. Patent 3,411,914, Kuwabara et al U.S. Patent 3,554,757, Oguchi et al U.S. Patent 3,565,631 and Oftedahl U.S. Patent 3,901,714, Kajiwara et al U.S. Patent 4,897,342, Yamada et al U.S. Patent 4,968,595, Yamada U.S. Patent 5,114,838, Yamada et al U.S. Patent 5,118,600, Jones et al U.S. Patent 5,176,991, Toyota et al U.S. Patent 5,190,855 and EPO 0 554 856, elemental sulfur as described by Miyoshi et al EPO 0 294,149 and Tanaka et al EPO 0 297,804, and thiosulfonates as described by Nishikawa et al EPO 0 293,917 and thiosulfonic acid as in MacIntyre et al U.S. Patent 5,411,855. Additionally or alternatively, the emulsions can be reduction-sensitized—e.g., with hydrogen, as illustrated by Janusonis U.S. Patent 3,891,446 and Babcock et al U.S. Patent 3,984,249, by low pH (e.g., less than 5), high pH (e.g., greater than 8) treatment, or through the use of reducing agents such as stannous chloride, thiourea dioxide, polyamines and amineboranes as illustrated by Allen et al U.S. Patent 2,983,609, Lowe et al U.S. Patents 2,518,698 and 2,739,060, Roberts et al U.S. Patents 2,743,182 and 1,83, Chambers et al U.S. Patent 3,026,203 and Bigelow et al U.S. Patent 3,361,564, Oftedahl et al Research Disclosure, Vol. 136, August, 1975, Item 13654. Yamashita et al U.S. Patent 5,254,456, EPO 0 407 576, Nelson et al U.S. Patent 5,283,168, Lok et al U.S. Patent 5,413,905, and Fujita et al U.S. Patent 5,420,004, and EPO 0 552 650. Klaus et al U.S. Patent 5,328,820 illustrates the use of sulfinate and disulfide during sensitization.

(2) Further illustrative of sulfur sensitization are Mifune et al U.S. Patent 4,276,374, Yamashita et al U.S. Patent 4,746,603, Herz et al U.S. Patents 4,749,646 and 4,810,626 and the lower alkyl homologues of these thioureas, Ogawa U.S. Patent 4,786,588, Ono et al U.S. Patent 4,847,187, Okumura et al U.S. Patent 4,863,844, Shibahara U.S. Patent 4,923,793, Chino et al U.S. Patent 4,962,016, Kashi U.S. Patent 5,002,866, Yagi et al U.S. Patent 5,004,680, Kajiwara et al U.S. Patent 5,116,723, Lushington et al U.S. Patent 5,168,035, Takiguchi et al U.S. Patent 5,198,331, Patzold et al U.S. Patent 5,229,264, Mifune et al U.S. Patent 5,244,782, East German DD 281 264 A5, German DE 4,118,542, EPO 0 302 251, EPO 0 363 527, EPO 0 371 338, EPO 0 447 105, Kojima et al U.S. Patent 5,266,457, and EPO 0 495 233. Further illustrative of iridium sensitization are Ihama et al U.S. Patent 4,693,965, Yamashita et al U.S. Patent 4,746,603, Kajiwara et al U.S. Patent 4,897,342, Leubner et al U.S. Patent 4,902,611, Kim U.S. Patent 4,997,751, Johnson et al U.S. Patent 5,164,292, Sasaki et al U.S. Patent 5,238,807, Uehida

U.S. Patent 5,399,476, Haefner et al U.S. Patent 5,391,474, Vaes et al EPO 0 679 934, and EPO 0 513 748. Further illustrative of tellurium sensitization are Sasaki et al U.S. Patent 4,923,794, Mifune et al U.S. Patent 5,004,679, Kojima et al U.S. Patent 5,215,880, EPO 0 541 104, Maruyama et al U.S. Patent 5,395,745, Sasaki et al U.S. Patent 5,393,655, Yoshida U.S. Patent 5,348,850, Sasaki et al EPO 0 661 589, Kashi et al EPO 0 573 649, Norawa et al EPO 0 572 662 and EPO 0 567 151. Further illustrative of selenium sensitization are Kojima et al U.S. Patent 5,028,522, Brugger et al U.S. Patent 5,141,845, Sasaki et al U.S. Patent 5,138,892, Yagihara et al U.S. Patent 5,236,821, Lewis U.S. Patent 5,240,827, EPO 0 428 041, EPO 0 443 453, EPO 0 454 149, EPO 0 458 278, EPO 0 506 009, EPO 0 512 496, Yamaya EPO 0 638 840, Takahashi EPO 0 652 471, Lok et al EPO 0 658 803, Suzuki EPO 0622 665, Suga U.S. Patent 5,397,692, Maskasky U.S. Patent 5,272,052, Yagihara et al U.S. Patent 5,306,613, and EPO 0 563 708. Further illustrative of rhodium sensitization are Grzeskowiak U.S. Patent 4,847,191 and EPO 0 514 675. Further illustrative of palladium sensitization are Ihama U.S. Patent 5,112,731, Szilcs et al U.S. Patent 5,169,751, East German DD 298 321 and EPO 0 368 304. Chromium sensitization is illustrated in Ikari et al EPO 0 658 802. Further illustrative of gold sensitizers are Mucke et al U.S. Patent 4,906,558, Miyoshi et al U.S. Patent 4,914,016, Mifune U.S. Patent 4,914,017, Aida et al U.S. Patent 4,962,015, Hasebe U.S. Patent 5,001,042, Tanji et al U.S. Patent 5,024,932, Deaton U.S. Patents 5,049,484 and 5,049,485, Ikenoue et al U.S. Patent 5,096,804, EPO 0 439 069, EPO 0 446 899, EPO 0 454 069 and EPO 0 564 910. The use of chelating agents during finishing is illustrated by Klaus et al U.S. Patent 5,219,721, Mifune et al U.S. Patent 5,221,604, EPO 0 521 612 and EPO 0 541 104. Illustrative of iron finishing is Ito et al U.S. Patent 5,420,001 and Marchetti et al U.S. Patent 5,264,336.

(3) Chemical sensitization can take place in the presence of spectral sensitizing dyes as described by Philippaerts et al U.S. Patent 3,628,960, Koiron et al U.S. Patent 4,439,520, Dickerson U.S. Patent 4,520,098; Maskasky U.S. Patent 4,693,965, Ogawa U.S. Patent 4,791,053 and Daubendiek et al U.S. Patent 4,639,411, Metoki et al U.S. Patent 4,925,783, Reuss et al U.S. Patent 5,077,183, Morimoto et al U.S. Patent 5,130,212, Fickie et al U.S. Patent 5,141,846, Kajiwara et al U.S. Patent 5,192,652, Asami U.S. Patent 5,230,995, Hashi U.S. Patent 5,238,806, East German DD 298 696, EPO 0 354 798, EPO 0 509 519, EPO 0 533,033, EPO 0 556 413, Nomiya EPO 0 572 012, Friour et al WO 95/17701, Deprez et al EPO 0 590 715, and EPO 0 562 476. Chemical sensitization can be directed to specific sites or crystallographic faces on the silver halide grain as described by Haugh et al U.K. Patent 2,038,792, Maskasky U.S. Patent 4,439,520, Maskasky U.S. Patent 5,275,930, Maskasky U.S. Patent 5,272,052, Iwagaki EPO 0 588 313, and Mifune et al EPO

0 302 528. The sensitivity centers resulting from chemical sensitization can be partially or totally occluded by the precipitation of additional layers of silver halide using such means as twin-jet additions or PAG cycling with alternate additions of silver and halide salts as described by Morgan U.S. Patent 3,917,485, Becker U.S. Patent 3,966,476 and Research Disclosure, Vol. 181, May 1979, item 18155. Also as described by Morgan cited above, Hasegawa U.S. Patent 5,411,849, Inoue et al. U.S. Patent 5,376,521, Waki U.S. Patent 5,286,622, Cole U.S. Patent 5,273,873, Kondo et al. EPO 0 645 668, the chemical sensitizers can be added prior to or concurrently with the additional silver halide formation. Chemical sensitization can take place during or after halide conversion as described by Hasebe et al. EPO 0 273 404.

(4) During finishing bromide, as illustrated by Ogawa U.S. Patent 4,786,588, Ohshima U.S. Patent 5,284,745, and Shiba et al. U.S. Patent 5,057,402, chloride as illustrated by EPO 0 438 135 and WO 92/10785, or iodide as illustrated by Takada et al. U.S. Patent 5,240,824 may be added to the emulsion. Urea compounds also may be added as illustrated by Burgmaier et al. U.S. Patent 4,810,626 and Adin U.S. Patent 5,210,002. The use of N-methyl formamide in finishing is illustrated in Reber EPO 0 423 982. The use of ascorbic acid and a nitrogen containing heterocycle are illustrated in Nishikawa EPO 0 378 841. Sensitization of core-shell emulsions is illustrated by Becker et al. U.S. Patent 4,495,277, Ikeda et al. U.S. Patent 4,985,350, Kato U.S. P. 5,306,608, Verbeeck et al. EPO 0 649 052, and EPO 0 272 675. The use of hydrogen peroxide in finishing is disclosed in Mifune et al. U.S. Patent 4,681,838.

(5) Sensitization may be affected by controlling gelatin to silver ratio as in Vandenberghe EPO 0 528 476 or by heating prior to sensitizing as in Berndt East German DD 298 319.

## V. Spectral sensitization and desensitization

### A. Sensitizing dyes

(1) The silver halide emulsions can be spectrally sensitized with dyes from a variety of classes, including the polymethine dye class, which includes the cyanines, merocyanines, complex cyanines and merocyanines (i.e., tri-, tetra- and polynuclear cyanines and merocyanines), oxonols, hemioxonols, styryls, merostyryls, streptocyanines, hemicyanines and arylidenes.

(2a) The cyanine spectral sensitizing dyes include, joined by a methine linkage, two basic heterocyclic nuclei, such as those derived from quinolinium, pyridinium, isoquinolinium, 3H-indolium, benz[e]indolium, oxazolium, thiazolium, selenazolinium, imidazolium, benzoxazolinium, benzothiazolium, benzoselenazolinium, benzimidazolium, naphthoxazolium, naphthothiazolium, naphthoselenazolinium, thiazolinium, dihydronaphthothiazolium, pyrylium and imidazopyrazinium quaternary salts. The

basic heterocyclic nuclei can also include tellurazoles or oxatellurazoles as described by Gunther et al. U.S. Patents 4,575,483, 4,576,905 and 4,599,410. Varied cyanine dyes, including varied substituents, are described in Parton et al. U.S. Patents 4,871,656 (heptamethine dyes with sulfoethyl or carboxyethyl nitrogen substituents) and 4,975,362 (infrared sensitizer with mercapto substituents), Ficken et al. U.S. Patent 4,996,141 (simple cyanine with particular substituents on a thiazole ring), Lea U.S. Patent 4,835,096 (cyanine infrared photothermographic sensitizers with cyclic ether substituents on benzo rings), Tanaka et al. U.S. Patent 4,940,657 (iodide substituent on cyanine, merocyanine or trinuclear dye), Matsunaga et al. U.S. Patent 5,223,389 (with aromatic polycyclic substituents), Anderson et al. U.S. Patent 5,210,014 (benzimidazoles with methyl, methylthio, fluoromethyl or fluoromethylthio substituents), Hinz et al. U.S. Patent 5,254,455 (5-fluoro substituted pentamethine benzothiazoles), Parton et al. U.S. Patent 5,091,298 (sulfo substituted carbamoyl nitrogen substituents), Burrows et al. U.S. Patent 5,216,166 (bridge nitro containing substituent), MacIntyre et al. U.S. Patent 5,135,845 (fluoro substituted), Ikegawa et al. U.S. Patent 5,198,332 (trimethine benzoazoles with substituents defined by STERIMOL parameter), Parton et al., US patent 5,316,904 (amide substituent), Parton US Patent 5,354,651 (hydroxy arylacyl substituent), Inagaki US Patent 5,387,502 (alkylthio substituent), Stegman et al. US Patent 5,418,126 (furan or pyrrole substituent), Fujiwara EPO 0 622 423 (benzimidazolocarbo-cyanine dyes with various substituents), Inagaki et al. EPO 0 638 841 (amide or sulfonamide substituent), Inagaki et al. EPO 0 652 472 (5-bromo-substituted simply cyanine dyes), Kagawa et al. EPO 0 362 387 (sulfo substituent on benzo or naphtho back ring) and EPO 0 521 632 (benzothiazole with alkoxy substituents), Hioki et al. EPO 0 443 466 (with aromatic polycyclic substituent), 0 474 047 (with aromatic polycyclic substituent), and 0 647 878 (aromatic polycyclic substituent). Ikegawa et al. EPO 0 530 511 (nitrogen sulfonamide or carbonamide type substituents), Nagaoki et al. EPO 0 534 283 (dyes with various particular emulsions), Kawata et al. EPO 0 565 121 (with nitrogen substituents cleavable upon processing to reduce residual color), Benard et al. WO 93/08505 (with macrocyclic thioether substituents) and Parton EPO 0 599 384 (substituent having specified Log P).

(2b) Cyanine dyes with carbocyclic rings in the methine chain linking nuclei are described in Lea et al. U.S. Patent 4,959,294 (Cl or Br substituent on bridging ring), Sato et al. U.S. Patent 4,999,282, Muentzer et al. U.S. Patent 5,013,642 (fused bridging rings), Parton et al. U.S. Patent 5,108,882 (fused bridging rings), Hioki et al. U.S. Patents 5,166,047 (also includes merocyanines with carbocyclic bridging ring), 5,175,080, and 4,939,080, Parton et al. U.S. Patent 5,061,618, Sakai U.S. Patent 5,089,382, Suzumoto et al. U.S. Patent 5,252,454, Patzold et al.

EPO 0 317 825, Burrows et al EPO 0 465 078 (with nitro substituent or bridging carbocyclic or heterocyclic ring), Kato (et al) EPO 0 532 042 and EPO 0 559 195 (6-membered bridging ring with one substituent), Kato US Patent 5,338,657, Kioki US Patent 5,356,769 (carbocyclic or heterocyclic ring), and Fabricius US Patent 5,330,884 (thioaryl substituent on carbocyclic ring).

(2c) Trinuclear type dyes which have a general cyanine type structure but with a heterocyclic nucleus in the bridging methine chain are described in Arai et al U.S. Patent 4,945,036, Mee et al U.S. Patent 4,965,183, Ono U.S. Patent 4,920,040 (trinuclear, cyanine structure with intermediate heterocyclic ring), Koya et al U.S. Patent 5,250,692, Bolger et al U.S. Patent 5,079,139, Kaneko et al U.S. Patent 5,234,806, Itoh et al EPO 0 642 005, Fich et al EPO 650 086, Deprez EPO 0 626 614, Delporta et al EPO 0 607 478 and Asami et al EPO 0 615 159 (carbocyclic or heterocyclic structure).

(2d) Cyanine dyes which have an indole nucleus are illustrated by Proehl et al U.S. Patent 4,876,181, Usagawa et al U.S. Patent 5,057,406, Kaneko et al U.S. Patents 5,077,186 and 5,153,114, Proehl et al EPO 0 251 282 and Fichen et al U.K. Patent 2,235,463.

(3) The merocyanine spectral sensitizing dyes include, joined by a methine linkage, a basic heterocyclic nucleus of the cyanine-dye type and an acidic nucleus such as can be derived from barbituric acid, 2-thiobarbituric acid, rhodanine, hydantoin, 2-thiohydantoin, 4-thiohydantoin, 2-pyrazolin-5-one, 2-isoxazolin-5-one, indan-1,3-dione, cyclohexan-1,3-dione, 1,3-dioxane-4,6-dione, pyrazolin-3,5-dione, pentan-2,4-dione, alkylsulfonyl acetonitrile, malononitrile, isouquinolin-4-one, and chroman-2,4-dione. The merocyanine dyes may include telluracyclohexanedione as acidic nucleus as described in Japanese Patent Application JA 51/136,420. Merocyanine type dyes are described in Fabricius et al U.S. Patents 5,108,887, and 5,102,781, Link U.S. Patent 5,077,191, Callant et al U.S. Patent 5,116,722, Hasebe et al US Patent 5,350,665, Diehl et al EPO 0 446,845, Ito et al EPO 0 540 295 (trinuclear merocyanine) and U.K. Patent 2,250,298, Kagawa et al EPO 0 614 114 (trinuclear merocyanine) and Deprez EPO 0 626 614. Other patents of interest are Ukai et al 5,294,709, Ikegawa et al U.S. Patent 5,338,656 and Delprato et al U.S. Patent 5,442,236.

(4) Additional types of sensitizing dyes include those described in Hioki et al U.S. Patents 4,814,265 (azulene nucleus) and 5,003,077 (methine dyes with a cycloheptimidazole nucleus), Fabricius US Patent 5,275,928 (methine dyes with pyrazolone nucleus), Okazaki et al U.S. Patent 4,839,269 (dyes with two or more cyclodextran groups), Wheeler U.S. Patent 4,614,801 (cyanine dyes with an indolizine nucleus), Burrows et al U.S. Patent 4,857,450 (hemicyanines), Roberts et al U.S. Patent 4,950,587 (dye polymers), Tabor et al U.S. Patent 5,051,351 (dye polymers).

with repeating amino acid units) and Inagaki et al U.S. Patent 5,183,733, Mee EPO 0 512 483 (hemicyanines).

(5a) One or more spectral sensitizing dyes may be used. Dyes with sensitizing maxima at wavelengths throughout the visible and infrared spectrum and with a great variety of spectral sensitivity curve shapes are known. The choice and relative proportions of dyes depends upon the region of the spectrum to which sensitivity is desired and upon the shape of the spectral sensitivity curve desired. Dyes with overlapping spectral sensitivity curves will often yield in combination a curve in which the sensitivity at each wavelength in the area of overlap is approximately equal to the sum of the sensitivities of the individual dyes. Thus, it is possible to use combinations of dyes with different maxima to achieve a spectral sensitivity curve with a maximum intermediate to the sensitizing maxima of the individual dyes. Combinations of sensitizing dyes which have sensitivities which do not necessarily overlap substantially, can be used on the same emulsion, such as illustrated by the black and white variable contrast element described in Henry et al EPO 0 536 769 and Ogawa U.S. Patent 5,114,837, which describes a red sensitized emulsion with an additional green and/or blue sensitizing dye present to provide tone reproducibility. Other patents of interest are: Mihara et al U.S. Patent 5,288,604, Inagaki U.S. Patent 5,310,630, Hasebe et al U.S. Patent 5,330,887, and Suga et al U.S. Patent 5,436,121.

(5b) Photographic elements, typically using one or more sensitizing dyes, having particular relationships of sensitivities at specified wavelength or wavelength ranges, are described in Matejec et al U.S. Patent 4,770,980 and EPO 0 409 019, Kitchen et al U.S. Patent 4,824,770, Shimazaki et al U.S. Patents 5,206,124 and 5,206,126 and EPO 0 447 138, Yamada et al U.S. Patent 5,252,444 and EPO 0 502 491, Nozawa U.S. Patent 5,166,042, Ohtani et al U.S. Patent 5,200,308, Fukazawa et al U.S. Patent 5,180,657, Waki et al U.S. Patent 5,084,374, Sasaki (et al) U.S. Patents 5,077,182 and 5,053,324, Shiba et al U.S. Patent 5,037,728, Inagaka US Patent 5,310,630, Bohan US Patent 5,434,038, Sakuma et al EPO 0 264 788, Nozawa EPO 0 377 463, Fukazawa et al EPO 0 434 044, Arakatsu et al EPO 0 452 853, Shimba et al EPO 0 458 315 and EPO 0 503 549, Tobita et al EPO 0 481 422, Uezawa et al EPO 0 501 465, Ikeda et al EPO 0 531 759, Hall EPO 0 550 110, Schmuck et al EPO 0 515 873, Brust et al WO 92/11574 and U.K. Patent 2,243,924.

(5c) Elements having specified gradients at peak spectral sensitivities are described in Sasaki et al EPO 0 324 471.

(6a) Combinations of spectral sensitizing dyes can be used which result in supersensitization--that is, spectral sensitization greater in some spectral region than that from any concentration of one of the dyes alone or that which would result from the additive effect of the dyes. Supersensitization can be

achieved with selected combinations of spectral sensitizing dyes and other addenda such as stabilizers and antifoggants, development accelerators or inhibitors, coating aids, brighteners and anti-static agents. Any one of several mechanisms, as well as compounds which can be responsible for supersensitization, are discussed by Gilman, *Photographic Science and Engineering*, Vol. 18, 1974, pp. 418-430. Examples of dye combinations said to provide supersensitization are provided in Ikegawa et al U.S. Patents 4,970,141 (trimethine benzoxazole with a substituent of oxazole cyanine dye) and 4,889,796, Asano et al U.S. Patent 5,041,366, Okumura et al U.S. Patent 5,292,633 (combination of red and green sensitizing dyes), Ikegawa et al U.S. Patents 5,308,748 and 5,310,645 (combination of dyes to improve residual color), Kim et al U.S. Patent 5,340,711 (combination of three green sensitizing dyes), Nishigaki U.S. Patent 5,389,505 (emulsion layer contain a combination sensitized with two dyes imparts interimage effect to a red sensitive layer), Schmuck et al U.S. Patent 5,437,972 (combination of dye for improved sensitivity and residual color), Dobles et al EPO 0 472 004 (two cyanine dyes with particular log P & oxidation and reduction potentials), Kawabe EPO 0 514 105 (three cyanine dyes, two being symmetric but with differing nuclei and one being asymmetric), Vaes et al EPO 0 545 453 (infrared sensitizer and red sensitizing cationic dye), Vaes et al EPO 0 545 452 (merocyanine or cyanine dye plus complex merocyanine), Irie et al U.S. Patent 5,49,986 (trimethine benzothiazole with alkoxy substituent plus triamethine benzothiazole or benzeneselenole), Miyake et al EPO 0 563 860 (infrared sensitized emulsion with two bridged cyanine dyes), Adin et al EPO 0 608 955 (combination of two green sensitizing dyes for sensitizing tabular grains).

(6b) Examples of addenda said to provide supersensitization or enhance speed, are provided in Philip et al U.S. Patent 4,914,015 (thio or oxy thiazoles added), Mihara U.S. Patent 4,965,182 (infrared cyanine sensitizers plus tetraazaindene), Tanaka et al U.S. Patent 4,863,846 (dyes plus inorganic sulfur), Sills et al U.S. Patent 4,780,404 (thiazoles for infrared sensitized emulsions), Momoki et al U.S. Patent 4,945,038 (bridged benzothiazoles plus bis-triazinyl compounds), Takahashi et al U.S. Patent 4,910,129 (triazole or tetrazole mercapto compounds), Gingello et al U.S. Patent 4,808,516 (added rhodamine), Ikeda et al U.S. Patent 4,897,343 (sensitized emulsion plus alkali metal sulfite and ascorbic acid), Davies et al U.S. Patent 4,988,615 (infrared sensitized emulsion plus Group V salt), Okusa et al U.S. Patent 5,166,046 (cyanine dye plus specific styrene substituted benzoles), Goedeweck U.S. Patent 5,190,854, Okuyama et al U.S. Patent 5,246,828 (red sensitized emulsion with macrocyclic compounds), Beltrami et al U.S. Patent 5,212,056 (blue dye plus disulfide compound), Arai et al U.S. Patent 5,229,262 (zero

methine merocyanine plus heterocyclic mercapto compound), Mihara et al U.S. Patent 5,149,619 (infrared cyanine sensitizer plus aromatic-carbamoyl or azole salts), Bucci et al U.S. Patent 5,232,826 (thiazole compounds), Simpson et al U.S. Patent 5,013,622 (added metal chelating agents), Philip Jr. et al U.S. Patent 5,306,612 (thiazoles), Franke et al U.S. Patent 5,443,948 (sulfate containing compound or polymeric compound) Friedrich et al U.S. Patent 5,009,992 (infrared sensitizers plus aromatic thiosulfonic acid or salt), Ishiguro et al U.S. Patent 5,260,183 (thiocyanate and tetraazaindene), Bucci et al EPO 0 440 947 (infrared sensitized emulsion with 1-aryl 5-mercaptotetrazole), Moriya et al EPO 0 445 648 (cyanine dye plus phenyl pyrazolone), Fabricius et al EPO 0 487 010 (zeromethine merocyanine plus tetraazaindene), Yamada et al German OLS 4,002,016 (infrared sensitizer plus betaine), and Deprez EPO 0 626 614 (salt of Group IIA metal) and Dewanckele et al EPO 0 609 571.

(7) Compounds used with sensitizing dyes to enhance other attributes of their performance include compounds to reduce coloration by residual sensitizing dyes as in Mishigaki et al EPO 0 426 193 or Kawai et al U.S. Patent 4,894,323 (rhodamine compound), metal complexes to inhibit dye desorption as in Ohzeki EPO 0 547 568, thiazole quaternary salt compounds to improve color reproduction with monomethine cyanine dyes in Ito et al U.S. Patent 5,024,928, acrylate or acrylamide polymers to reduce sensitizing dye stain as in Schofield et al WO 91/19224, dye bis-triazinyl compounds to reduce the width of sensitization as in Tanemura et al U.S. Patent 4,556,633, bis-aminostilbenes and ascorbic acid to reduce desensitization from dyes as in Ikeda et al U.S. Patent 4,917,997 use of an oxamide-containing compound to improve dot quality as in Kolorich U.S. Patent 5,306,598 and compounds to reduce variations in sensitivity or other properties during coating, standing, or as a result of storage or processing conditions as in Ohbayashi et al U.S. Patent 4,818,671 (high chloride emulsion sensitized with gold, sulfur and limited amount of monomethine benzothiazole), Kojima et al U.S. Patent 4,839,270, Gilman et al U.S. Patent 4,933,273, Goda U.S. Patent 5,037,733, Hioki et al U.S. Patent 5,192,654, Tanaka et al U.S. Patent 5,219,722, Asami U.S. Patent 5,244,779, Lenhard et al U.S. Patent 5,037,734, Otani U.S. Patent 5,043,256, Suzumoto et al U.S. Patent 0 313 021, Hall EPO 0 351 077, Waki EPO 0 368 356, Kobayashi et al EPO 0 402 087 and Ogawa EPO 0 421 464. Other combinations include those in Ikeda et al U.S. Patent 4,837,140 (various sensitizing dyes on element having up to 0.78 g/m<sup>2</sup> of silver as silver halide) and Tanaka et al U.S. Patent 5,081,006 (high chloride emulsion having benzothiazole cyanine with benzo- or naphtho-selenazole or thiazole dye, and phenolic cyan coupler).

(8) Spectral sensitizing dyes also affect the emulsions in other ways. For example, many spectrally sensitizing dyes either reduce (desensitize) or increase photographic

speed within the spectral region of inherent sensitivity. Spectral sensitizing dyes can also function as antifogants or stabilizers, development accelerators or inhibitors, reducing or nucleating agents, and halogen acceptors or electron acceptors, as disclosed in Brooker et al U.S. Patent 2,131,038, Illingsworth et al U.S. Patent 3,501,310, Webster et al U.S. Patent 3,630,749, Spence et al U.S. Patent 3,718,470, Shiba et al U.S. Patent 3,930,860, Saitou et al U.S. Patent 4,987,064, and Ikeda et al U.S. Patent 4,971,889.

(9) Dyes which desensitize negative-working silver halide emulsions are generally useful as electron-accepting spectral sensitizers for fogged direct-positive emulsions. Typical heterocyclic nuclei featured in cyanine and merocyanine dyes well-suited for use as desensitizers are derived from nitrobenzothiazole, 2-aryl-1-alkylindole, pyrrole[2,3-b]pyridine, imidazo[4,5-b]quinoxaline, carbazole, pyrazole, 5-nitro-3H-indole, 2-arylbenzindole, 2-aryl-1,8-trimethyleneindole, 2-heterocyclylindole, pyrylium, benzopyrylium, thiapyrylium, 2-amino-4-aryl-5-thiazole, 2-pyrrole, 2-(nitroaryl)indole, imidazo[1,2-a]pyridine, imidazo[2,1-b]thiazole, imidazo[2,1-b]-1,3,4-thiadiazole, imidazo[1,2-b]pyridazine, imidazo[4,5-b]quinoxaline, pyrrole[2,3-b]quinoxaline, pyrrole[2,3-b]pyrazine, 1,2-diarylindole, 1-cyclohexylpyrrole and nitrobenzoxazolinone. Such nuclei can be further enhanced as desensitizers by electron-withdrawing substituents such as nitro, acetyl, benzoyl, sulfonyl, benzosulfonyl and cyano groups.

(10) Sensitizing action and desensitizing action can be correlated to the position of molecular energy levels of a dye with respect to ground state and conduction band energy levels of the silver halide crystals. These energy levels can in turn be correlated to polarographic oxidation and reduction potentials, as discussed in Photographic Science and Engineering, Vol. 18, 1974, pp. 49-53 (Sturmer et al), pp. 175-178 (Leubner) and pp. 475-485 (Gilman). Oxidation and reduction potentials can be measured as described by R. J. Cox, Photographic Sensitivity, Academic Press, 1973, Chapter 15. Red sensitizing dyes of specified reduction potentials are described by Ohshima et al EPO 0 421 452.

(11) The chemistry of cyanine and related dyes is illustrated by Weissberger and Taylor, *Special Topics of Heterocyclic Chemistry*, John Wiley and Sons, New York, 1977, Chapter VIII; Venkatarāman, *The Chemistry of Synthetic Dyes*, Academic Press, New York, 1971, Chapter V; James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapter 8, and F. M. Hamer, *Cyanine Dyes and Related Compounds*, John Wiley and Sons, 1964 and "Polymethine Dyes, Structure and Properties" by N. Tyutuz'kov, J. Favian, A. Melhorn, F. Diety and A. Tadjer, St. Kliment Ohridski University Press 1991.

(12a) Among useful spectral sensitizing dyes for sensitizing silver halide emulsions are those found in U.K.

Patent 742,112, Brooker U.S. Patents 1,846,300, '301, '302, '303, '304, 2,078,233 and 2,089,729, Brooker et al U.S. Patents 2,165,338, 2,213,238, 2,493,747, '748, 2,526,632, 2,739,964 (Reissue 24,292), 2,778,823, 2,917,516, 3,352,857, 3,411,916 and 3,431,111, Sprague U.S. Patent 2,503,776, Nys et al U.S. Patent 3,282,933, Riester U.S. Patent 3,660,102, Kampfer et al U.S. Patent 3,660,103, Taber et al U.S. Patents 3,335,010, 3,352,680 and 3,384,486, Lincoln et al U.S. Patent 3,397,981, Fumia et al U.S. Patents 3,482,978 and 3,623,881, Spence et al U.S. Patent 3,718,470, Mee U.S. Patent 4,025,349 and Kofron et al U.S. Patent 4,439,510.

(12b) Examples of useful supersensitizing-dye combinations, of non-light-absorbing addenda which function as supersensitizers or of useful dye combinations are found in McFall et al U.S. Patent 2,933,390, Jones et al U.S. Patent 2,937,089, Motter U.S. Patent 3,506,443, and Schwan et al U.S. Patent 3,672,898. Among desensitizing dyes useful as spectral sensitizers for fogged direct-positive emulsions are those found in Kendall U.S. Patent 2,293,261, Coenen et al U.S. Patent 2,930,694, Brooker et al U.S. Patent 3,431,111, Mee et al U.S. Patents 3,492,123, 3,501,312 and 3,598,595, Illingsworth et al U.S. Patent 3,501,310, Lincoln et al U.S. Patent 3,501,311, Vanlare U.S. Patent 3,615,608, Carpenter et al U.S. Patent 3,615,639, Riester et al U.S. Patent 3,567,456, Jenkins U.S. Patent 3,574,629, Jones U.S. Patent 3,579,345, Mee U.S. Patent 3,582,343, Fumia et al U.S. Patent 3,592,653 and Chapman U.S. Patent 3,598,596.

(13) Spectral sensitizing dyes can be added at any stage during the emulsion preparation. They may be added at the beginning of or during precipitation as described by Wall, *Photographic Emulsions*, American Photographic Publishing Co., Boston, 1929, p. 65, Hill U.S. Patent 2,735,766, Philippaerts et al U.S. Patent 3,628,960, Locker U.S. Patent 4,183,756, Locker et al U.S. Patent 4,225,666 and *Research Disclosure*, Vol. 181, May, 1979, Item 18155, Tani et al EPO 0 301 508, and Tani et al U.S. Patent 4,741,995. They can be added prior to or during chemical sensitization as described by Kofron et al U.S. Patent 4,439,520, Dickerson U.S. Patent 4,520,098, Maskasky U.S. Patent 4,435,501, Philippaerts et al cited above, and Beltramini EPO 0 540 656. They can be added before or during emulsion washing as described by Asami et al EPO 0 287 100, Metoki et al EPO 0 291 399 and Leichsenring East German DD 288 251. The dyes can be mixed in directly before coating as described by Collins et al U.S. Patent 2,912,343. They can be added at controlled temperatures of 50-80°C as in Urata U.S. Patent 4,954,429, or for defined mixing times as in Takiguchi EPO 0 460 800, or in specific solvents as in Tani U.S. 5,192,653, in controlled amounts as in Hiroaki et al Japanese patent application JP 4 145 429 and Price et al U.S. patent 5,219,723.

(14) Small amounts of halide ion that forms a silver halide less soluble than that of the grains (e.g., Br<sup>-</sup> or I<sup>-</sup> on AgCl grains or I<sup>-</sup> on AgBr grains) can be adsorbed to the emulsion grains to promote aggregation and adsorption of the spectral sensitizing dyes as described by UK Patent 1,413,826 and Kofron et al U.S. Patent 4,439,520. Post-processing dye stain can be reduced by the proximity to the dyed emulsion layer of fine high-iodide grains as described by Dickerson U.S. Patent 4,520,098. Depending on their solubility, the spectral sensitizing dyes can be added to the silver halide emulsion as solutions in water or solvents such as methanol, ethanol, acetone or pyridine, dissolved in surfactant solutions as described by Sakai et al U.S. Patent 3,822,135 or as dispersions as described by Owens et al U.S. Patent 3,469,987 and Japanese Patent Application 24185/71. The dyes can be selectively adsorbed to particular crystallographic faces of the emulsion grain, as a means of restricting chemical sensitization centers to other faces, as described by Mifune et al EPO 0 302 528. Substituents which can perform additional photographic functions such as direct-positive nucleation or development acceleration can be included in the dye structure, as described by Spence et al U.S. Patents 3,718,470 and 3,854,956. Research Disclosure, Vol. 151, November, 1976, Item 15162, and Okazaki et al U.S. Patent 4,800,154. The spectral sensitizing dyes may be used in conjunction with poorly adsorbed luminescent dyes, as described by Miyasaka et al U.S. Patents 4,908,303, 4,876,183 and 4,820,606, EPO 0 270 079, EPO 0 270 082 and EPO 0 278 510 and Sugimoto et al U.S. Patent 4,963,476.

#### B. Desensitizers

The silver halide emulsions can include desensitizers which are not dyes, such as N,N'-dialkyl-4,4'-bispyridinium salts, nitron and its salts, thiuram disulfide, piazine, nitro-1,2,3-benzothiazole, nitroindazole and 5-mercaptopotetrazole, as illustrated by Peterson et al U.S. Patent 2,271,229, Kendall et al U.S. Patent 2,541,472, Abbott et al U.S. Patent 3,295,976, Rees et al U.S. Patents 3,184,313 and 3,403,025, Gibbons et al U.S. Patent 3,922,545, Sumi et al U.S. Patent 4,666,827, Uesawa et al U.S. Patent 4,840,889, and Pietsch et al East German DD 298 969.

#### VI.

**UV dyes/optical brighteners/luminescent dyes**  
(1) Ultraviolet absorbing dyes for use in photographic elements include those described by Besio et al U.S. Patent 4,849,326 (cyano substituted butamines), Logan U.S. Patent 4,839,274 (acetylenic compounds), Pruett et al U.S. Patent 5,215,876 (substituted styrenes), the hydroxyphenylbenzotriazoles of Nishijima et al EPO 0 451 813, Schofield et al EPO 0 190 003, and Umemoto U.S. Patent 5,084,375 and Leppard et al EPO 0 531 258 (triazines).

(2) Optical brightening agents can be employed in the photographic elements, as is generally reviewed by Roosens, *Photographic Korrespondenz*, Vol. 94, No. 1, pp. 3-11, and No. 2, pp. 19-26 (1958). The brightening agents can include thiophenes as illustrated by Tuite et al U.S. Patent 3,449,257 and Crawford U.S. Patent 3,501,298, stilbenes as illustrated by Tomko et al U.S. Patent 4,794,071, Saunders U.S. Patent 3,260,715, Wirth et al U.S. Patent 2,581,057, Williams et al U.S. Patent 2,618,636 and James U.K. Patent 672,803, triazines as illustrated by Williams et al U.S. Patent 2,713,046 and van der Grinten Dutch Patent 74109, imidazolones as illustrated by Sargent U.S. Patent 2,571,706 and Libby et al U.S. Patent 2,723,197, pyrazolines as illustrated by Kendall et al U.K. Patents 669,590 and 712,764, and Nishio U.S. Patent 5,143,822, triazoles as illustrated by Williams et al U.S. Patent 2,623,064, Baum et al U.S. Patent 2,713,054 and Sartori U.S. Patent 2,715,630, coumarins as illustrated by Sartori U.S. Patent 2,702,296 and Gold et al German Patent 911,369, acetynes as illustrated by Meyer German OLS 2,525,680, oxazoles and oxadiazoles as illustrated by Heidke U.S. Patent 3,513,102, vinylene compounds as illustrated by Tuite U.S. Patents 3,788,854 and 3,789,012, and Leppard et al EPO 0 359 710, and phthalocyanines as illustrated by Delfino U.S. Patent 5,213,951. These and other brighteners, as well as methods of improving their stability, are illustrated by Tuite U.S. Patent 3,684,729. Ballasted optical brighteners are described in Adin U.S. Patent 5,395,748. Water-soluble brighteners can be dispersed directly in hydrophilic colloid layers of the photographic elements, as is further illustrated by U.K. Patent 440,032 and McFall et al U.S. Patent 2,933,390, while hydrophobic brighteners can be dispersed in a manner similar to other hydrophobic photographic addenda, as further illustrated by Koerber et al U.S. Patents 3,047,390, 3,181,949 and '950, Pattijn et al U.S. Patent 3,359,102, Knott et al U.S. Patent 3,434,837, Oetiker et al U.S. Patent 3,406,070 and Janssen German Patent 1,150,274.

Chen U. S. Patent 4,203,716 discloses the incorporation of hydrophobic brighteners in photographic elements by the use of loaded latex compositions in which the brightener is dispersed in polymer particles of a latex. Incorporation of hydrophobic brighteners in hydrophilic layers of photographic elements by a process in which brightener is incorporated in polymer particles by a suspension polymerization technique and the resulting polymer particles are dispersed in a hydrophilic binder is disclosed in Remley U. S. Patent 4,584,255. Capturing agents for retaining fluorescent whiteners in the photographic element during processing are described in Sasaki et al EPO 0 286 331.

#### VII. Antifoggants and stabilizers

(1) Instability which increases minimum density in negative-type emulsion coatings (i.e., fog) or which increases



minimum density or decreases maximum density in direct-positive emulsion coatings can be protected against by incorporation of stabilizers, antifogants, antinkinking agents, latent-image stabilizers and similar addenda in the emulsion and contiguous layers prior to coating. Most of the antifogants effective in emulsions can also be used in developers and can be classified under a few general headings, as illustrated by C.E.K. Nees, *The Theory of the Photographic Process*, 2nd Ed., Macmillan, 1954, pp. 677-680.

(2) To avoid such instability in emulsion coatings with conventional, tabular, and structured halide grains, stabilizers and antifogants can be employed, such as halide ions (e.g., bromide salts), chloropalladates and chloropalladites as illustrated by Trivelli et al U.S. Patent 2,566,263, water-soluble inorganic salts of magnesium, calcium, cadmium, cobalt, manganese and zinc as illustrated by Jones U.S. Patent 2,839,405 and Sidebotham U.S. Patent 3,488,709, mercury salts as illustrated by Allen et al U.S. Patent 2,728,663, selenols and diselenides as illustrated by Brown et al U.K. Patent 1,336,570 and Pollet et al U.K. Patent 1,282,303, quaternary ammonium salts of the type illustrated by Allen et al U.S. Patent 2,694,716, Brooker et al U.S. Patent 2,131,038, Graham U.S. Patent 3,342,596, Arai et al U.S. Patent 3,954,478, and Lok U.S. Patent 5,232,827, azomethine desensitizing dyes as illustrated by Thiers et al U.S. Patent 3,630,744, isothiourea and cyclic thiourea derivatives as illustrated by Herz et al U.S. Patent 3,220,839, Knott et al U.S. Patent 2,514,650, and Öhlschlager et al U.S. Patent 3,565,625, peptide derivatives as illustrated by Scavron U.S. Patent 3,274,002, pyrimidines and 3-pyrazolidones as illustrated by Welsh U.S. Patent 3,161,515, Hood et al U.S. Patent 2,751,297, Kok et al U.S. Patent 5,156,940, and Heremans et al EPO 0 528 480, polyhydroxyalkyl compounds as illustrated by Lok et al U.S. Patent 5,370,986, triazoles and tetrazoles as illustrated by Baldassarri et al U.S. Patent 3,925,086, Sakamoto et al U.S. Patent 4,871,658, Vetter et al U.S. Patent 5,006,457, and Öhlschlager et al German OLS 4,007,731, azaindenes, particularly tetraazaindenes, as illustrated by Helmback U.S. Patent 2,444,605, Knott U.S. Patent 2,933,388, Williams U.S. Patent 3,202,512, *Research Disclosure*, Vol. 134, June, 1975, Item 13452, and Vol. 148, August, 1976, Item 14851, and Nepker et al U.K. Patent 1,338,567, rhodanine compounds as illustrated by Link et al U.S. 5,429,919, polymeric thioethers as illustrated by Dewanckele EP 674,215 mercaptotetrazoles, -triazoles and -diazoles as illustrated by Kendall et al U.S. Patent 2,403,927, Kennard et al U.S. Patent 3,266,897, *Research Disclosure*, Vol. 116, December, 1973, Item 11684, Luckey et al U.S. Patent 3,397,987, Salesin U.S. Patent 3,708,303, Öhlschlager U.S. Patent 4,804,623, Hirano et al 5,290,674, Miyayashi et al 5,284,740, Delprato et al EPO 600,308, Loiacono et al EPO 644,458, Krauss et

al EPO 0 330 018, and Tanaka et al EPO 0 564 281, azoles as illustrated by Peterson et al U.S. Patent 2,271,229 and *Research Disclosure*, Item 11684, cited above, purines as illustrated by Sheppard et al U.S. Patent 2,319,090, Birr et al U.S. Patent 2,152,460, *Research Disclosure*, Item 13452, cited above, and Dostes et al French Patent 2,296,204, polymers of 1,3-dihydroxy-(and/or 1,3-carbamoxy)-2-methyleneisopropane as illustrated by Saleck et al U.S. Patent 3,926,635 and tellurazoles, tellurazolinines, tellurazolinium salts and tellurazolinium salts as illustrated by Gunther et al U.S. Patent 4,661,438, aromatic oxatelurazolinium salts as illustrated by Gunther, U.S. Patent 4,581,330 and Przyklek-Elting et al U.S. Patents 4,661,438 and 4,677,202, telluroethers as illustrated by Sasaki et al U.S. Patent 4,923,794, combinations of a uracil and a nitroso-substituted phenol as described by Beebe et al U.S. Patent 4,430,426, fluoroaromatics as described by Sakamoto et al U.S. Patent 4,741,990, N-acyl-cysteines as described by Wagner et al German OLS 3,838,467, N-acyl sulfanamides as described by Japanese Patent Application JP 2/272,445, dichalcogenides as described by Boettcher et al U.S. Patent 5,217,859 and Klaus et al U.S. Patent 5,219,721, water soluble disulfides as described in Budz et al U.S. 5,418,127; phenylmercaptotetrazoles as described by Himmelwright et al U.S. Patent 4,888,273; Heinecke et al U.S. 5,374,505 and McIntyre et al U.S. Patent 4,957,855, mercaptazoles as described by Becker et al U.S. Patent 4,906,557, Hayashi U.S. Patent 5,187,053, Hirano et al U.S. Patent 5,242,791, Ito et al EPO 0 462 579, and Baba et al U.K. Patent Application 2,216,279, benzo-bisthiazole quaternary salts as described by Delprato U.S. Patent 4,849,327, organic oxidants as described by Brown U.S. Patent 4,468,454, selenoethers as described by Kojima et al U.S. Patent 5,028,522, organic acids as described by Bergthaller et al EPO 0 362 604, sulfonic acids as described by Okushima et al U.S. Patent 4,863,843, a combination of macrocyclic compounds and mercapto compounds as described in Ohya et al EPO 601,393, palladium compounds as described in Cellone et al EPO 597,312; hydrazones as described by Hioki et al U.S. 5,409,809; hydrazine compounds as described by Fabricius et al EPO 652,470, and various combinations as described by Becker et al U.S. Patent 5,089,381. High-chloride emulsions can be stabilized by the presence, especially during chemical sensitization, of elemental sulfur as described by Miyoshi et al EPO 0 294 149 and Tanaka et al EPO 0 297 804 and thiosulfonates as described by Nishikawa et al U.S. Patent 4,960,689, combinations of a thiosulfonate and a sulfinate as described by Lok U.S. Patents 5,292,635 and 5,399,479, combinations of a polysulfide and a nitrogen containing heterocyclic as described in Kajiwara et al U.S. Patent 5,116,723, combinations of a diamino disulfide and a sulfinate as described by Lok et al U.S.



Patent 5,356,770; combinations of sulfur donating compounds and sulfinate as described by Lok EPO 655,643; combinations of sulfur donating compounds and phosphine compounds as described by Lok U.S. Patent 5,415,992; and thiosulfonate/sulfinate compounds as described by Lok U.S. Patent 5,443,947. A method of adding stabilizers and antifogants to an emulsion is described in Fodor et al EPO 568,950.

(3) Among useful stabilizers for gold sensitized emulsions are water-insoluble gold compounds of benzothiazole, benzoxazole, naphthothiazole and certain merocyanine and cyanine dyes, as illustrated by Yutzy et al U.S. Patent 2,597,915, and sulfonamides, as illustrated by Nishio et al U.S. Patent 3,498,792.

(4) Among useful stabilizers in layers containing poly(alkylene oxides) are tetraazaindenes, particularly in combination with Group VIII noble metals or resorcinol derivatives, as illustrated by Carroll et al U.S. Patent 2,716,062, U.K. Patent 1,466,024 and Habu et al U.S. Patent 3,929,486, quaternary ammonium salts of the type illustrated by Piper U.S. Patent 2,886,437, water-insoluble hydroxides as illustrated by Maffet U.S. Patent 2,953,455; phenols as illustrated by Smith U.S. Patents 2,955,037 and '038, ethylene diurea as illustrated by Dersch U.S. Patent 3,582,346, barbituric acid derivatives as illustrated by Wood U.S. Patent 3,617,290, boranes as illustrated by Bigelow U.S. Patent 3,725,078, aromatic hydroxyl compounds as illustrated by Sills EPO 0 339 870, 3-pyrazolidinones as illustrated by Wood U.K. Patent 1,158,059, and aldoximes, amides, anilides and esters as illustrated by Butler et al U.K. Patent 988,052.

(5) The emulsions can be protected from fog and desensitization caused by trace amounts of metals such as copper, lead, tin, iron and the like by incorporating addenda such as sulfocatechol-type compounds, as illustrated by Kennard et al U.S. Patent 3,236,652, aldoximes as illustrated by Carroll et al U.K. Patent 623,448 and meta- and polyphosphates as illustrated by Draibach U.S. Patent 2,239,284, and carboxylic acids such as ethylenediamine tetraacetic acid as illustrated by U.K. Patent 691,715.

(6) Among stabilizers useful in layers containing synthetic polymers of the type employed as vehicles and to improve covering power are monohydric and polyhydric phenols as illustrated by Forsgard U.S. Patent 3,043,697, saccharides as illustrated by U.K. Patent 897,497 and Stevens et al U.K. Patent 1,039,471, and quinoline derivatives as illustrated by Dersch et al U.S. Patent 3,446,618.

(7) Among stabilizers useful in protecting the emulsion layers against dichroic fog are addenda such as salts of nitron as illustrated by Barbier et al U.S. Patents 3,679,424 and 3,820,998, mercaptocarboxylic acids as illustrated by Willems et al U.S. Patent 3,600,178, and addenda listed by E. J. Birr,

Stabilization of Photographic Silver Halide Emulsions, Focal Press, London, 1974, pp. 126-218.

(8) Among stabilizers useful in protecting emulsion layers against development fog are addenda such as azabenzimidazoles as illustrated by Bloom et al U.K. Patent 1,356,142 and U.S. Patent 3,575,699, Rogers U.S. Patent 3,473,924 and Carlson et al U.S. Patent 3,649,267, substituted benzimidazoles, benzothiazoles, benzotriazoles and the like as illustrated by Brooker et al U.S. Patent 2,131,038, Land U.S. Patent 2,704,721, Rogers et al U.S. Patent 3,265,498, mercapto-substituted compounds, e.g., mercaptotetrazoles, as illustrated by Dimsdale et al U.S. Patent 2,432,864, Rauch et al U.S. Patent 3,081,170, Weyerts et al U.S. Patent 3,260,597, Grasshoff et al U.S. Patent 3,674,478, Arond U.S. Patent 3,706,557, and Koide et al U.S. Patent 5,151,357, isothiourea derivatives as illustrated by Herz et al U.S. Patent 3,220,839, thiodiazole derivatives as illustrated by von Konig U.S. Patent 3,364,028 and von Konig et al U.K. Patent 1,186,441, nitrogen substituted heterocycles as illustrated by Kojima et al U.S. Patent 5,192,647, thiosulfonate derivatives as illustrated by Shuto et al U.S. Patent 5,110,719, and masked benzotriazoles as illustrated by Kok et al U.S. Patent 5,254,443.

(9) Where hardeners of the aldehyde type are employed, or the material is exposed to aldehyde compounds, the emulsion layers can be protected with antifogants such as monohydric and polyhydric phenols of the type illustrated by Sheppard et al U.S. Patent 2,165,421, nitro-substituted compounds of the type disclosed by Rees et al U.K. Patent 1,269,288, poly(alkylene oxides) as illustrated by Valbusa U.K. Patent 1,151,914, muco-halogenic acids in combination with urazoles as illustrated by Allen et al U.S. Patents 3,232,761 and 3,232,764, or further in combination with maleic acid hydrazide as illustrated by Rees et al U.S. Patent 3,295,980, pyrazolone compounds of the type described by Nagaoka et al U.S. Patent 5,248,586, soluble halides as described by Reuss et al U.S. Patent 5,021,336, hydrophobic hardener scavengers as described by Riecke et al EPO 0 575 910, and the compounds described by Sugimoto et al U.S. Patent 4,581,329 and Shibahara EPO 0 477 932.

(10) To protect emulsion layers coated on linear polyester supports, addenda can be employed such as parabanic acid, hydantoin acid hydrazides and urazoles as illustrated by Anderson et al U.S. Patent 3,287,135, and pyrazines containing two symmetrically fused 6-member carbocyclic rings, especially in combination with an aldehyde-type hardening agent, as illustrated in Rees et al U.S. Patent 3,396,023.

(11) Kink or pressure desensitization of the emulsions can be reduced by the incorporation of thallous nitrate as illustrated by Overman U.S. Patent 2,628,167, compounds, polymeric lattices and dispersions of the type disclosed by Jones et al U.S. Patents 2,759,821 and '822, azole and mercaptotetrazole

hydrophilic colloid dispersions of the type disclosed by Research Disclosure, Vol. 116, December, 1973, Item 11684, plasticized gelatin compositions of the type disclosed by Milton et al U.S. Patent 3,033,680, water-soluble interpolymers of the type disclosed by Rees et al U.S. Patent 3,536,491, polymeric latices (alkylene oxide) as disclosed by Pearson et al U.S. Patent 3,772,032, gelatin graft copolymers of the type disclosed by Rakoczy U.S. Patent 3,837,861, the organic thioethers or tetra-substituted thioureas of Suga et al U.S. Patent 5,015,567, and the compounds of Sasaki et al EPO 0 488 029.

(12) Where the photographic element is to be processed at elevated bath or drying temperatures, as in rapid access processors, pressure desensitization and/or increased fog can be controlled by selected combinations of addenda, vehicles, hardeners and/or processing conditions as illustrated by Abbott et al U.S. Patent 3,295,976, Barnes et al U.S. Patent 3,545,971, Salesin U.S. Patent 3,708,303, Yamamoto et al U.S. Patent 3,615,619, Brown et al U.S. Patent 3,623,873, Taber U.S. Patent 3,671,258, Abele U.S. Patent 3,791,830, Research Disclosure, Vol. 99, July, 1972, Item 9930, Florens et al U.S. Patent 3,843,364, Priem et al U.S. Patent 3,867,152, Adachi et al U.S. Patent 3,967,965, Mikawa et al U.S. Patents 3,947,274 and 3,954,474, Okutsu et al U.S. Patent 4,435,500, Ohashi et al U.S. Patent 4,920,043, Kajiwara et al U.S. Patent 4,830,955, Miyoshi et al U.S. Patent 4,839,263, Hirabayashi et al U.S. Patent 4,892,807, Nishijima et al U.S. Patent 4,954,431, Okumura et al U.S. Patent 4,994,362, Uesawa et al EPO 0 253 585, Delfino EPO 0 467 106, and Kase EPO 0 542 306.

(13) In addition to increasing the pH or decreasing the pH of an emulsion and adding gelatin, which are known to retard latent-image fading, latent-image stabilizers can be incorporated, such as amino acids, as illustrated by Ezekiel U.K. Patents 1,335,923, 1,378,354, 1,387,654 and 1,391,672, Ezekiel et al U.K. Patent 1,394,371, Jefferson U.S. Patent 3,843,372, Jefferson et al U.K. Patent 1,412,294 and Thurston U.K. Patent 1,343,904, carbonyl-bisulfite addition products in combination with hydroxybenzene or aromatic amine developing agents as illustrated by Seiter et al U.S. Patent 3,424,583, cycloalkyl-1,3-diones as illustrated by Beckett et al U.S. Patent 3,447,926, enzymes of the catalase type as illustrated by Matejec et al U.S. Patent 3,600,182, halogen-substituted hardeners in combination with certain cyanine dyes as illustrated by Kumai et al U.S. Patent 3,881,933, hydrazides as illustrated by Honig et al U.S. Patent 3,386,831, alkenyl benzothiazolium salts and thiazolium salts as illustrated by Arai et al U.S. Patent 3,954,478, Beltramini et al U.S. Patent 4,780,400, Lok et al EPO 0 410 753, Bonheyo et al EPO 0 488 030 and EPO 0 490 297, hydroxy-substituted benzylidene derivatives as illustrated by Thurston U.K. Patent 1,308,777 and Ezekiel et al U.K. Patents 1,347,544 and

1,353,527, mercapto-substituted compounds of the type disclosed by Sutherns U.S. Patent 3,519,427, metal-organic complexes of the type disclosed by Matejec et al U.S. Patent 3,639,128, penicillin derivatives as illustrated by Ezekiel U.K. Patent 1,389,089, propynylthio derivatives of benzimidazoles, pyrimidines, etc., as illustrated by von Konig et al U.S. Patent 3,910,791, combinations of iridium and rhodium compounds as disclosed by Yamasue et al U.S. Patent 3,901,713, sydnone or sydnone imines as illustrated by Noda et al U.S. Patent 3,881,939, thiazolidine derivatives as illustrated by Ezekiel U.K. Patent 1,458,197, thioether-substituted imidazoles as illustrated by Research Disclosure, Vol. 136, August, 1975, Item 13651, polysulfides as illustrated by Makoto et al EPO 0 447 105, disulfides as illustrated by Berghaller German OLS 3,922,202, combinations of a mercapto compound and a chalcogazolium compound as illustrated by Becker EPO 0 377 889, and polyhydroxy aromatic compounds as illustrated by Lok et al EPO 0 335 107; cysteine as illustrated by Pätzold et al DE 4,227,749 and the compounds illustrated by Kawashima et al EPO 611 109.

(14) Among stabilizers useful in protecting emulsion layers against pressure fog and scratch sensitivity are addenda such as hydrazides as illustrated by Fiechowski et al U.S. Patent 5,244,772, hydroquinone derivatives as illustrated by Toya et al EPO 0 476 521, Takada et al EPO 0 482 599, Maruyama et al EPO 0 488 029, and Sasaoka et al EPO 0 452 772, and the use of low levels of sensitizing dye in combination with specific antifogants as described in Irving et al EPO 0 566 075.

## VIII.

### Absorbing and scattering materials

Incident radiation can be specularly transmitted, reflected, scattered or absorbed, depending upon the choice of materials forming the photographic element layers. Specular transmission relies upon similar refractive indices of layers and components forming interfaces and is essential to obtaining sharp images. Reflective or absorbing materials incorporated directly in the silver halide emulsion layers can increase speed or sharpness. Filter materials, typically located in overcoat and interlayers, can trim spectrally or attenuate incident radiation and antihalation materials, typically located in undercoat and backing layers, can eliminate or diminish reflection (halation) exposure of emulsion layers.

#### A. Reflective materials

The reflective materials in the silver halide emulsion layers can include pigments of high refractive index as illustrated by Marriage U.K. Patent 504,283 and Yutzy et al U.K. Patent 760,775, reflecting undercoat layers containing silver halide as illustrated by Russell U.S. Patent 3,140,179, or silver halide grains sized to optimize scattering as illustrated by Locker U.S. Patent 3,989,527. Sutton et al U.S. Patent 5,300,413 discloses tabular grain emulsions with low thickness coefficients

of variation to obtain light reflection in selected wavelength regions, but ultrathin (<0.07 µm) tabular grains, disclosed by Antoniadou et al. U.S. Patent 5,250,403, are not spectrally selective in reflectance and exhibit minimal reflectance at thicknesses less than about 0.03 µm.

#### B. Absorbing materials

(1) Absorbing materials can include filter and anti-halation dyes such as the pyrazolone oxonol dyes of Gaspar U.S. Patent 2,274,782 and Adachi et al. U.S. Patent 4,833,246; Diehl et al. U.S. Patent 4,877,721; Tanaka et al. U.S. Patent 4,904,578; Ohno et al. U.S. Patent 4,933,268; Kawashima et al. U.S. Patent 4,960,686; Murai et al. U.S. Patent 4,996,138; Waki et al. U.S. Patent 5,057,404 (with phenolic or naphtholcyan couplers); Kuwashima et al. U.S. Patents 5,091,295 (pyrazolones) and 5,204,236; Momoki et al. U.S. Patent 5,326,161 (used with amido or carbamoyl substituted hydroxyphenyl compounds); Tai et al. U.S. Patent 5,388,908; Kawashima et al. U.S. Patent 5,476,928. Further absorber dyes include the solubilized diaryl azo dyes of Van Campen U.S. Patent 2,956,879; Fujiwara et al. U.S. Patent 4,871,655; Kitchin et al. U.S. Patent 4,977,961 (azomethines), the solubilized styryl and butadienyl dyes of Heseltine et al. U.S. Patents 3,423,207 and 3,384,487, the merostyryl dyes of Diehl U.S. Patent 2,723,723, the merocyanine dyes of Silberstein et al. U.S. Patent 2,527,583 and Ohno U.S. Patent 5,223,382 (with chromanone nucleus), Adachi et al. U.S. Patent 5,434,026; Callant et al. U.S. Patent 4,889,973; Jimbo et al. U.S. Patent 5,130,305 (isoxazole containing methine dyes) and U.S. Patent 5,486,897; Kieken et al. U.S. Patent 5,312,724, the merocyanine and oxonol dyes of Oliver (et al) U.S. Patents 3,486,897, 3,652,284 and 3,718,472 and the enaminohemioxonol dyes of Brooker et al. U.S. Patent 3,976,661. Other patents of interest are: Masukawa et al. U.S. Patent 4,788,284; Diehl et al. U.S. Patent 5,283,165; Harada et al. U.S. Patent 5,312,724; Fabricius et al. U.S. Patent 5,330,884; Ohnishi et al. U.S. Patent 5,340,707; Yamada et al. U.S. Patent 5,370,980; Harada U.S. Patent 5,368,022; Harada U.S. Patent 5,312,723; Harada U.S. Patent 5,312,722; Matsushita et al. U.S. Patent 5,272,050; Usagawa et al. U.S. Patent 5,390,977; Kieken et al. U.S. Patent 5,286,748; Harada et al. U.S. Patent 5,380,145; Kawai et al. U.S. Patent 5,643,328; Kieken et al. U.S. Patent 5,656,401; Warlishi et al. U.S. Patent 5,665,271; Blavasco et al. U.S. Patent 5,655,645.

(2) Ultraviolet absorbers are also known, such as the cyanomethyl sulfone-derived merocyanines of Oliver U.S. Patent 3,723,154, the thiazolidones, benzotriazoles and thiazolochiazoles of Sawdey U.S. Patents 2,739,888, 3,253,921 and 3,250,617; Sawdey et al. U.S. Patent 2,739,971; Hirose et al. U.S. Patent 4,783,394; Takahashi U.S. Patent 5,200,307; Tanji et al. U.S. Patent 5,112,728, and Leppard et al. U.S. Patent 5,323,408; Liebe et al. U.S. Patent 5,363,820; Roth East German DD 288,249, the triazoles of Heller et al. U.S. Patent 3,004,896, the hemioxonols of Wahl et al. U.S. Patent 3,125,597 and Weber et al. U.S. Patent 4,045,229, the

acidic substituted methine oxonols of Diehl et al. U.S. Patent 5,553, the triazines of Leppard et al. U.S. Patent 5,520,938 and U.S. Patent 5,530,135, as well as the other UV absorbers of Liebe et al. U.S. Patent 5,514. Other patents of interest are: Toan U.S. Patent 5,489,503; Falk et al. U.S. Patent 5,387,691; Falk et al. U.S. Patent 5,439,955; Prestel et al. U.S. Patent 5,276,161; Chen et al. U.S. Patent 5,384,235; Schofield et al. U.S. Patent 5,383,815, and Hasebe U.S. Patent 5,571,935.

(3) The dyes and ultraviolet absorbers can be mordanted as illustrated by Jones et al. U.S. Patent 3,282,699 and Heseltine et al. U.S. Patents 3,455,693, 3,438,779 and Foss et al. U.S. Patent 5,169,747.

(4) Absorbing dyes can be added as particulate dispersions, as described by Lemahieu et al. U.S. Patent 4,092,168; Diehl et al. WO 88/04795 and U.S. Patent 4,274,723, and Factor et al. U.S. Patent 5,299,435. Additional particulate dispersions of absorbing dyes are described in Factor et al. U.S. Patent 4,900,653; Diehl et al. U.S. Patent 4,940,654 (dyes with groups having ionizable protons other than carboxy); Factor et al. U.S. Patent 4,948,718 (with arylpyrazolone nucleus); Diehl et al. U.S. Patent 4,950,586; Anderson et al. U.S. Patent 4,988,611 (particulates of particular size ranges and substituent pKa values); Diehl et al. U.S. Patent 4,994,356; Usagawa et al. U.S. Patent 5,208,137; Adachi U.S. Patent 5,213,957 (merocyanines); Usami U.S. Patent 5,238,798 (pyrazolone oxonols); Usami et al. U.S. Patent 5,238,799 (pyrazolone oxonols); Diehl et al. U.S. Patent 5,213,956 (tricyanopropenes and others); Inagaki et al. U.S. Patent 5,075,205; Otp et al. U.S. Patent 5,098,818; Texter U.S. Patent 5,274,109 and 5,326,687 (microprecipitated methine oxonol dyes); McManus et al. U.S. Patent 5,098,820; Inagaki et al. U.S. Patent 3,855,461; Fujita et al. U.S. Patent 5,423,693; Usui U.S. Patent 5,423,742 (containing groups with specific pKa values); Usagawa et al. U.S. Patent 5,434,413 (pyrazolones with particular sulfamoyl, carboxyl and similar substituents); Jimbo et al. U.S. Patent 5,460,550; Diehl et al. U.S. Patent 5,524,593 (having alkoxy or cyclic ether substituted phenyl substituents); Diehl et al. U.S. Patent 5,524,594 (furan substituted phenyl substituents); Diehl et al. U.S. Patent 5,526,454; Harada et al. U.S. Patent 5,260,178; Diehl et al. U.S. Patent 5,260,179; Ohya et al. U.S. Patent 5,262,289; Diehl et al. U.S. Patent 5,266,454; Inoue et al. U.S. Patent 5,260,178; Diehl et al. U.S. Patent 5,300,394 (solid particle dispersions milled in presence of fluorosurfactant); Idogaki U.S. Patent 5,356,766; Inoue et al. U.S. Patent 5,366,845; Miller et al. U.S. Patent 5,468,598 (solid particle dispersion milled in presence of water-spluble or water dispersible polymer); Czekai et al. U.S. Patent 5,478,705 (milling solid particle dyes with polymeric milling media); Czekai et al. U.S. Patent 5,500,331 (milling solid particle dyes with small particle milling media); Vandenabeele et al. U.S. Patent 5,569,074 (precipitated dispersions in presence of silica

sol), Yamamoto et al. EPO 0 646 836, Haraga et al. EPO 0 613 048, Ohya EPO 0 594 973, Taguchi EPO 0 679 935.

(5) Absorbing dyes can absorb infrared radiation, as described by Proehl et al. EPO 0 251 282, Parton et al. EPO 0 288 076, and Japanese Patent Application JA 62/123454. Further infrared absorbing dyes are described in Parton et al. U.S. Patent 4,933,269 (cyanines with carbocyclic ring in bridge), Hall et al. U.S. Patent 5,245,045 (heptamethine oxonols), Harada EPO 0 568 857. Particular infrared absorbing dyes include those of the cyanine type with indole nuclei such as described in West et al. U.S. Patent 5,107,063, Laganis et al. U.S. Patent 4,882,265, Harada et al. EPO 0 430 244, Parton et al. EPO 0 288 076, Delprato et al. EPO 0 523 465, Delprato et al. EPO 0 539 786 (indolotri-carbocyanines with bridge amine substituents) and Harada EPO 0 568 022. Other patents of interest are: Kiekens et al. 5,420,281, Kiekens et al. U.S. Patent 5,362,612, Fabricius et al. U.S. Patent 5,397,690, Inagaki U.S. Patent 5,310,630, Katoh et al. U.S. Patent 5,326,686, Biavasco et al. EPO 0 655 645, and Callant et al. EPO 0 586 749.

(6) Absorbing dyes having specific substituents intended to assist in their removal during processing by solubilization, oxidation or other methods, are described in Yagihara et al. U.S. Patent 4,923,789, Harder et al. U.S. Patent 5,158,865, Karino et al. U.S. Patent 5,188,928, Kawashima et al. EPO 0 409 117 (particular amido, ureido, and the like solubilizing groups), Matsushita EPO 0 508 432 and Mooberry et al. WO 92/21064. Other patents of interest are: Karino U.S. Patent 5,278,037, Kiekens et al. U.S. Patent 5,344,749, Kiekens et al. U.S. Patent 5,380,634, Taguchi EPO 0 679 935, Kiekens et al. EPO 0 675 403.

(7) Various other azo type dyes are described in Matejec et al. U.S. Patent 5,108,883 (azomethines), Jimbo U.S. Patent 5,155,015 (arylaazoxazolinones or arylazobutenolides), Motoki et al. U.S. Patent 5,214,141 (azomethines with N-aryl substituents and cyclic amino group), Yamazaki U.S. Patent 5,216,169 (hydroxypyrideneazomethines) and Fabricius WO 93/13458 (diketo diazo dyes).

(8) Other absorber dyes are described in Masukawa et al. U.S. Patent 4,788,284 (diphenylimidazoles), Ohno et al. U.S. Patent 4,920,031 (pyridone oxonols), Shuttleworth et al. U.S. Patent 4,923,788 (furanones), Kuwashima et al. U.S. Patent 4,935,337 (pyridone oxonols), Carlier et al. U.S. Patent 5,187,282 (xanthene derivatives), Loer et al. EPO 0 329 491 (trinuclear cyanine with methine bridge having acidic nucleus of type in oxonol or merocyanine dyes), Usagawa et al. EPO 0 342 939 (indolq-cyanines with acid solubilizing groups on back rings), Adachi et al. EPO 0 366 145 (pyrazoloazoles), Suzuki et al. EPO 0 518 238 (pyrazolotriazoles), Usagawa et al. EPO 0 521 664 (silver salts of various dyes), Hirabayashi et al. EPO 0 521 668 (silver salts of various dyes), Kawashima et al. EPO 0 521 711 (silver salts of pyrimidine containing compounds) and Hall EPO 0 552 010.

(9) Absorbing dyes or dye combinations used to obtain absorption at particular wavelengths, manner of incorporating them in a photographic element, or absorbing dyes plus other components, are described in Alliet et al. U.S. Patent 4,770,984 (location of absorber dyes), Szajewski U.S. Patent 4,855,220 (dye absorbing in region to which layer underneath is sensitized), Toya et al. U.S. Patent 5,147,769 (dye in oil droplet dispersion or polymer latex), Stockel et al. U.S. Patent 5,204,231 (absorber dye combinations for various wavelengths of absorption), Schofield et al. U.S. Patent 5,372,922 (polymeric ultraviolet absorbers loaded with high boiling organic solvents), Toda et al. U.S. Patent 5,393,648 (filter dyes dispersed with high molecular weight condensation polymers), Okada et al. EPO 0 319 999 (yellow absorber dye plus colloidal silver), Harada et al. EPO 0 412 379, Ohno et al. EPO 0 445 627 (dye combinations), Karino EPO 0 456 163 (location and dye amounts), Murai et al. EPO 0 510 960, Kawai et al. EPO 0 539 978. Other patents of interest are: Bowne U.S. Patent 5,298,377, Nakagawa et al. U.S. Patent 5,348,846, Sasai et al. U.S. Patent 5,401,820, Adin et al. U.S. Patent 5,298,379, Heremans EPO 0 681 209, Alliet et al. EPO 0 582 000, Iwasaki et al. EPO 0 690 342, Slater et al. EPO 0 646 839, and Roland et al. EPO 0 666 500.

#### C. Discharge

The materials can be discharged (i.e., decolorized or solubilized) in photographic processing solutions (e.g., alkaline, bleaching and/or fixing solutions) or by alkaline vapor, heat or light processing as illustrated by Altman U.S. Patent 3,289,839, Mitchell U.S. Patent 3,619,194, Wiese et al. U.S. Patent 3,769,019, Heseltine et al. U.S. Patent 3,745,009 (Reissue 29,168) and Sturmer U.S. Patent 3,984,248.

### IX. Coating physical property modifying addenda

#### A. Coating aids

(1) The photographic element layers can contain various types of coating aids (e.g., wetting agents) such as anionic, cationic, nonionic or zwitterionic surfactants, alone or in combination. Some useful coating aids are saponin; alkylamine oxides as described in Knox U.S. Patent 3,607,291; sulfonated alkylaryl polyethers as illustrated by Baldaiefen U.S. Patent 2,600,831, Knox et al. U.S. Patents 2,719,087 and 3,026,202, Sakamoto et al. U.S. Patent 4,192,683 and Nishio et al. U.S. Patent 3,415,649; alkylene glycol ethers of polyhydric alcohols as disclosed by Swan et al. U.S. Patent 2,240,469, Swan U.S. Patent 2,240,472, Knox et al. U.S. Patent 2,831,766; Seidel et al. U.S. Patent 3,409,435, Eisenman et al. U.S. Patent 3,442,654, Knox U.S. Patent 3,514,293, Padday U.S. Patent 3,516,844, Gantz et al. U.S. Patent 3,617,292, Wagner et al. U.K. Patent 774,806, U.K. Patent 1,022,878 and Milton U.K. Patent 1,201,054; amphoteric compounds as described in McQueen U.S. Patent 2,197,809, Chilton U.S.

Patent 2,368,287, Gates U.S. Patent 2,824,015, Swan U.S. Patent 2,240,471, Knox et al U.S. Patents 2,992,108, 3,091,623, 3,169,870 and 3,306,749, Harriman U.S. Patent 3,018,178, Ben-Ezra U.S. Patent 3,133,816, Wolf et al U.S. Patent 3,408,193, Nighio et al U.S. Patents 3,441,413 and 3,545,974, Sato et al U.S. Patent 3,475,174, Knox U.S. Patent 3,506,449, Gantz et al U.S. Patent 3,563,756, Kalenda U.S. Patent 3,573,049, Mackey U.S. Patent 3,619,199, Yamamoto et al U.S. Patents 3,726,683 and 3,843,368; carboxyalkyl-substituted polyglycol ethers and esters as described in Ville et al U.S. Patent 3,663,229; various types of monoesters derived from polyhydroxy compounds as disclosed in Boomer U.S. Patent 2,190,645, Swan U.S. Patent 2,240,470, Simmons U.S. Patent 2,240,475, Swan et al U.S. Patent 2,353,279, Knox et al U.S. Patent 3,220,847, Hagge et al U.S. Patent 3,516,833 and U.K. Patent 1,012,495; fluoro-substituted compounds as illustrated by McDowell U.S. Patent 3,589,906, Groh et al U.S. Patent 3,666,478, Babbitt et al U.S. Patent 3,775,126, Bailey et al U.S. Patent 3,850,642, Habu et al German OLS 2,610,485, U.K. Patent 1,439,402, and Cruikshank et al, Research Disclosure, Vol. 166, February, 1978, Item 16630; imidazoles as illustrated by Mackey U.S. Patent 2,982,651 and Knox U.S. Patent 3,539,352; maleo-pimarates, optionally in combination with an acetylenic ethylene oxide derivative, or a sucrose ester of an aliphatic acid, as disclosed in Knox et al U.S. Patent 2,823,123, Wilson et al U.S. Patent 3,041,171 and Knox U.S. Patents 3,437,485 and 3,564,576; maleic ester amides as illustrated in Kamio U.S. Patent 4,547,459; the sodium salt of the condensation product of naphthalene sulfonic acid and formaldehyde as illustrated in Salminen et al U.S. Patent 3,062,649; phosphate esters of glycidol polyethers as disclosed in Mackey U.S. Patent 3,725,079; poly(dimethylsiloxane) as described in Hughes et al U.S. Patent 3,885,965; long-chain sucrose ethers or urethanes as illustrated by Nishio et al U.S. Patent 3,507,660; higher alcohol sulfates, water-soluble (sulfo) salts of the aliphatic esters of succinic acid, fatty acid esters of hydroxyalkyl sulfonic acid, amide and ester derivatives of sulfoacetic acid, alpha-sulfo lower alkyl esters of 7 to 18 carbon atom fatty acids and sulfate ester products of a glycidol polyether as described in Baldisieff U.S. Patent 2,203,768, Simmons et al U.S. Patent 2,240,476, Harsh et al U.S. Patent 2,447,462, Knox et al U.S. Patents 3,068,101 and 3,201,252, Mackey et al U.S. Patent 3,516,835, Mackey U.S. Patent 3,725,080, Pollet et al U.S. Patent 3,793,032, Ishihara et al U.S. Patent 3,824,102 and Research Disclosure, Vol. 160, August, 1977, Item 16040; sulfoxides as described by Herz, Research Disclosure, Vol. 129, September, 1975, Item 12927; combinations of alkyl sulfate surfactants and N-acyl sarcosinate surfactants as disclosed in Cruikshank et al U.S. Patent 4,370,412; taurines as disclosed by Knox et al U.S. Patents 2,739,891 and 3,165,409 and Ben-Ezra U.S. Patent 3,042,522. These and other suitable coating aids are disclosed in

McCutcheons's Detergents and Emulsifiers, Allured Publishing Corp., 1973.

(2) Relatively recent coating aids, surfactants and dispersing agents, including anionic, nonionic and cationic materials are described in Furlan et al U.S. Patent 5,037,729, Cavallo et al U.S. Patent 5,098,821, Ashida et al U.S. Patent 5,008,150, Toya (et al) U.S. Patents 4,916,049 and 4,920,032, Yoneyama et al U.S. Patent 4,916,054, Pitt et al U.S. Patents 4,968,599 and 4,988,610 and WO 91/18321, Briggs et al U.S. Patent 4,892,806, Ishigaki U.S. Patent 5,208,139, Yoneyama et al U.S. Patent 5,221,603, Uesawa et al U.S. Patent 4,762,776, Orem U.S. Patent 5,411,844, Fujita et al U.S. Patent 5,415,986, Orem U.S. Patent 5,418,128, Endres et al German OLS 3,835,077, Mochizuki et al EPO 0 556 002, Fukazawa et al EPO 0 306 245, Takada et al EPO 0 567 083, Tachibana et al EPO 0 361 138, Orem EPO 0 549 496, Ueda et al EPO 0 643 327 and Vandenaesle EPO 0 644 455.

#### B. Plasticizers and lubricants

(1) The flexibility of the silver halide emulsion and other hydrophilic colloid-containing layers of the elements upon drying can be improved through the incorporation of plasticizers. Representative plasticizers include alcohols, dihydric alcohols, trihydric alcohols and polyhydric alcohols, acid amides, cellulose derivatives, lipophilic couplers, esters, phosphate esters such as tricresyl phosphate, glycol esters, diethylene glycol mixed esters, phthalate esters such as dibutyl phthalate and butyl stearate, tetraethylene glycol dimethyl ether, ethyl acetate copolymers, lactams, lower alkyl esters of ethylene bis-glycolic acid, ether esters or diesters of an alkylene glycol or a polyalkylene glycol, polyacrylic acid esters, polyethylene imines, poly(vinyl acetate) and polyurethanes, as illustrated by Eastman et al U.S. Patent 306,470, Wiest U.S. Patent 3,635,853, Milton et al U.S. Patent 2,960,404, Faber et al U.S. Patent 3,412,159, Ishihara et al U.S. Patent 3,640,721, Illingsworth et al U.S. Patent 3,003,878, Lowe et al U.S. Patent 2,327,808, Umberger U.S. Patent 3,361,565, Gray U.S. Patent 2,865,792, Milton U.S. Patents 2,904,434 and 2,860,980, Milton et al U.S. Patent 3,033,680, Dersch et al U.S. Patent 3,173,790, Fowler U.S. Patent 2,772,166 and Fowler et al U.S. Patent 2,835,582, VanPasschen et al U.S. Patent 3,397,988, Balle et al U.S. Patent 3,791,857, Jones et al U.S. Patent 2,759,821, Ream et al U.S. Patent 3,287,289 and Dewinter et al U.S. Patent 4,245,036.

(2) The photographic elements can contain lubricants to reduce sliding friction encountered in use. Representative lubricants which can be used in photographic elements include long-chain fatty acids, alkali salts of sulfonated castor oil, alkaline earth metal salts of higher aliphatic carboxylic acids, monohydric and dihydric alcohols, ethers, primary amides, hydroxyalkyl amine fatty acid condensates, esters, polyesters, sperm-oil products, polysaccharide derivatives, polytetrafluoroethylene particles, colloidal silica, silicone derivatives, poly-

meric silicone compounds plus  $\delta$ -alanine-derivative surfactants, mixtures of an alkyl silicone and an aryl silicone, phosphate triesters, alkali metal salts of alkylphosphoric acid esters, poly(methyl methacrylate) beads, betaines, acyl alkyl taurines and paraffins and waxes such as carnauba wax, as illustrated by Guestaux et al U.S. Patents 3,082,087 and 3,658,573, Roblins U.S. Patent 2,588,765, Nellist et al U.K. Patent 1,263,722, Harriman U.S. Patent 3,018,178, Brown et al U.K. Patents 1,320,564 and 1,320,757, Duane U.S. Patent 3,121,060, DeBoer et al, Research Disclosure, Vol. 139, November, 1975, Item 13969, Mackey et al U.S. Patent 3,870,521, Stephens U.S. Patent 3,679,411, McGraw U.S. Patent 3,489,567, Ben-Ezra U.S. Patent 3,042,522, U.K. Patent 955,061, Tallet et al U.S. Patent 3,080,317, Earhart et al U.S. Patent 3,516,832, Knox et al U.S. Patent 2,739,891, Secrist et al U.S. Patent 3,295,979, Nadeau et al U.S. Patent 3,222,178 and Guestaux French Patent 2,180,465, Shibue et al U.K. Patent Application 2,027,221, Naol et al U.S. Patent 4,232,117 and Sugimoto et al U.S. Patent 4,675,278.

(3) Yoneyama et al U.S. Patent 5,063,147, Takeuchi U.S. Patent 5,019,491 Shiba et al U.S. Patent 4,866,469, Geiger et al U.S. Patent 5,288,602 and Miyamoto EPO 0 668 534 represent relatively recent publications relating to plasticizers and lubricants.

#### C. Antistats

(1) The photographic elements can contain conducting layers such as antistatic layers. Such layers can contain soluble salts such as chloride, nitrate and similar water soluble salts; conductive metals such as evaporated metals; conductive carbon as illustrated by Simmons U.S. Patent 2,327,828, insoluble inorganic salts such as those described by Trevo U.S. Patents 3,245,833 and 3,428,451, and polymers having ionic groups as illustrated by Minsk U.S. Patent 2,861,056, Sterman et al U.S. Patent 3,206,312, Babbitt et al U.S. Patent 3,775,126, Trevo U.S. Patents 3,963,498, 4,025,342, 4,025,463, 4,025,691 and 4,025,704, Smith U.K. Patent 1,466,600, Kelley et al Research Disclosure, Vol. 158, June, 1977, Item 15840, Campbell et al Research Disclosure, Vol. 162, October, 1977, Item 16258, and Mecca Research Disclosure, Vol. 166, February, 1978, Item 16630, combinations of inorganic salts and compounds comprising polyalkylene oxides as illustrated by Kishimoto U.S. Patent 4,272,616, Chen et al U.S. Patents 4,582,781 and 4,610,955, and Japanese Patent Application JA 62/293,241, polyalkylene oxide-substituted polyphosphazenes as illustrated by Japanese Patent Application JA 62/286,038, and combinations of complexes of polyalkylene oxide-substituted polyphosphazenes, as illustrated by Chen et al EPO 0 304 296 and Japanese Patent Application 62/286,038.

(2) Undesirable static discharges during manufacture, exposure and processing of photographic materials can also be controlled by modification of the surface-charging characteristics

tics of the emulsion or backing. Matting agents can reduce the electrostatic charging by reducing the effective area of surface making contact. Surfactants of various kinds and combinations can also be employed as illustrated by Defeast et al U.S. Patent 3,754,924, Bailey et al U.S. Patents 3,850,642 and 3,888,678, Babbitt et al U.S. Patents 3,775,126, 3,850,640 and 4,013,696; and U.K. Patent GB 1,330,356.

(3) Because most of the radiation from static electrical discharges is in the ultraviolet range, the photographic material can be protected from static exposure by the use of such UV-absorbing materials as yellow antihalation dyes and specific UV absorbers. The UV-absorbing materials can already be in place for purposes of antihalation or improved color rendition as described in Section VIII of this disclosure, or can be added for static protection as illustrated by Kondo et al German OLS 2,163,904.

(4) Relatively recent publications relating to antistatic agents and their use in photography are illustrated by Timmerman et al U.S. Patent 4,828,927, Vallarino U.S. Patent 4,863,801, Cho U.S. Patent 4,891,308, Aizawa et al U.S. Patent 4,895,792, Tachibana et al U.S. Patent 4,898,808, Besio et al U.S. Patent 4,914,018, Mukunoki et al U.S. Patent 4,917,993, Gundlach U.S. Patent 4,940,655, Chen et al U.S. Patent 4,948,720, Tachibana et al U.S. Patent 4,956,270, Cho U.S. Patent 4,960,687, Chen et al U.S. Patent 4,971,897, Cavallo et al U.S. Patent 4,975,363, Fujita et al U.S. Patent 4,978,602, Kuwabara et al U.S. Patent 4,999,276, Yamada et al U.S. Patent 5,004,669, Anderson et al U.S. Patent 5,006,451, Van Thillo et al U.S. Patent 5,008,178, Tsukada U.S. Patent 5,013,637, Mukunoki et al U.S. Patent 5,028,516, Cho et al U.S. Patent 5,077,185, Tachibana et al U.S. Patents 5,079,136, 5,084,339, 5,094,909 and 5,098,822, Shibata et al U.S. Patent 5,108,084, Beisswenger et al U.S. Patent 5,128,233, Takamuki et al U.S. Patent 5,135,843, Ueda et al U.S. Patent 5,137,802, Hirabayashi et al U.S. Patent 5,153,113, Yasunami et al U.S. Patent 5,153,115, Nagasaki et al U.S. Patent 5,173,396, Ueda et al U.S. Patent 5,209,985, Anderson et al U.S. Patent 5,221,598, Saverin et al U.S. Patent 5,232,824, Carlson U.S. Patent 5,236,818, Huffman U.S. Patent 5,238,706, Hosoi et al U.S. Patent 5,238,800, Ishigaki et al U.S. Patent 5,238,801, Bowman et al U.S. Patent 5,244,728, Tachibana et al U.S. Patent 5,284,741, Yamanouchi et al U.S. Patent 5,300,416, Melpolder et al U.S. Patent 5,308,687, Stimson et al 5,326,688, Anderson et al U.S. Patent 5,340,676, Carlson U.S. Patent 5,344,751, Quintens et al U.S. Patent 5,354,613, Havens et al U.S. Patent 5,356,468, Anderson et al U.S. Patent 5,360,706, Shiratsuchi et al U.S. Patent 5,362,613, Jones et al U.S. Patent 5,366,544, Anderson et al U.S. Patent 5,366,855, Christian et al U.S. Patent 5,368,995, Kurachi et al U.S. Patent 5,372,923, Quintens et al U.S. Patent 5,372,924, Kurachi et al U.S. Patent 5,376,517, Muys et al U.S. Patent 5,391,472, Morrison et al U.S.



Patent 5,427,835, Boston et al. U.S. Patent 5,439,785, Fornasari et al. U.S. Patent 5,441,860, Krafft et al. U.S. Patent 5,443,944, Ubel et al. EPO 0 250 154, Yoneyama et al. EPO 0 288 059, Van Gossum et al. EPO 0 296 656, Hesse et al. EPO 0 319 951, Tachibana et al. EPO 0 391 402, Habu et al. EPO 0 409 665, Arai et al. EPO 0 416 867, Tachibana et al. EPO 0 430 110, Van Thillo et al. EPO 0 444 326, Ito et al. EPO 0 452 102, Arai et al. EPO 0 476 429, Wada et al. EPO 0 476 453, Valsecchi et al. EPO 0 486 982, Milner EPO 0 504 826, Timmerman et al. EPO 0 505 626, Coltrain et al. EPO 0 531 006, Vandenberghe EPO 0 534 006, Ito et al. EPO 0 552 617, Kurachi et al. EPO 0 569 821, Valsecchi et al. EPO 0 589 329, Bayless et al. EPO 0 631 178, Furian et al. EPO 0 633 496, Vandenberghe EPO 0 644 456, Gardner EPO 0 646 837, Ballerini et al. EPO 0 647 879, Tsuji EPO 0 652 469, Valsecchi et al. EPO 0 655 646, Taguchi EPO 0 660 174, Cause U.K. Patent Application 2 246 870, Etile DE 41 03 437, Melpolder et al. WO 90/13851, Araki et al. EPO 0 476 429, Anderson et al. WO 91/18061 and WO 91/18062, Robert WO 93/06040, Tixier et al. WO 93/06043 and Bennett et al. WO 94/13477.

#### D. Matting Agents

(1) The layers of the photographic elements can contain matting agents for such purposes as prevention of blocking and ferrotyping, reduction of static charging and excessive sheen, physical durability, pencil acceptance, improved air release during vacuum drawdown and avoidance of Newton's rings. Finely divided inorganic particles such as various forms of silica, barium and calcium sulfates, zinc and titanium oxides, desensitized silver halide and zinc carbonate, dispersed in natural and synthetic vehicles, can be employed as illustrated by Robijns U.S. Patent 2,192,241, Maynard et al. U.K. Patent 1,201,905, deHaes U.S. Patent 3,257,206, Nadeau U.S. Patent, 3,437,484, Himmelmarm et al. U.S. Patent 3,322,555, Whitmore et al. U.S. Patent 3,411,907, Moede U.S. Patent 3,353,958, Hasenauer et al. U.S. Patent 3,370,951, Takenaka et al. U.S. Patent 3,615,554, U.K. Patent 1,260,772, Oshibuchi et al. U.S. Patent 3,635,714, Verburg U.S. Patent 3,769,020, Secrist et al. U.S. Patent 4,029,504, Nagatomo et al. U.S. Patent 4,021,245 and German OLS 2,529,321, Yutzy et al. U.K. Patent 760,775, Byerley et al. U.S. Patent 3,523,022 and Salminen et al. U.S. Patent 3,062,649.

(2) Finely divided organic particles or beads can be similarly used as matting agents, such as calcium organic salts, starches—including starch esters, flours, arrowroot, india rubber, talc, hardened deionized or deashed gelatin, zein and polymeric materials—including various forms of cellulose and polymers or copolymers of  $\alpha$ ,  $\beta$ -ethylenically unsaturated mono- and di-carboxylic acids; esters and half-esters and their sulfonic acid analogues (particularly acrylic and methacrylic acids and their methyl esters), styrene, acrylonitrile and fluorinated ethylenes, as well as polycarbonate and poly(vinyl alcohol), as

illustrated by Jelley U.S. Patent 1,939,213, Knoefel U.S. Patents 2,221,873 and 2,268,662, Lindquist U.S. Patent 2,322,037, Plakunov U.S. Patent 3,591,379, Potter et al. U.S. Patent 2,376,005, Jelley et al. U.S. Patent 2,992,101, Minsk et al. U.S. Patent 2,391,181, Lynn U.S. Patent 2,701,245, Earhart et al. U.S. Patent 3,516,832, Morcher et al. U.S. Patent 3,079,257, Grabhoefer et al. U.S. Patent 3,443,946, Klockgether et al. U.S. Patent 3,262,782, U.K. Patent 1,055,713, De Geest et al. U.S. Patent 3,754,924 and Hutton U.S. Patent 3,767,448. Vinyl chloride polymers or copolymers can be used as illustrated by Roth et al. U.K. Patent 2,033,596, copolymers of fluorinated monomers and silicon-containing monomers as described in Japanese Patent Application JA 62/17744, and copolymers of maleic anhydride and olefins as illustrated by Bruck et al. U.S. Patent 4,287,299. The matte can consist of inorganic particles coated with an organic polymer as illustrated by Thijs et al. U.S. Patent 4,235,959, of layered polymer particles, as illustrated in Japanese Patent Application JA 62/17742, or polymers coated with fluorine compounds, as illustrated in Japanese Patent Application JA 61/230136. The particle surfaces can be linked to gelatin, as illustrated by Bagchi et al. EPO 0 307 855.

(3) The matte particles may be of a range of sizes and of various shapes, for example, irregular as in the case of silica particles or spherical as in the case of many organic polymer mattes. The particles can be monodisperse as illustrated in Research Disclosure, Vol. 216, April, 1982, Item 21617. The particles can be porous, as illustrated by Naito, U.S. Patent 4,094,848. The matte particles can be pigmented or dyed, as illustrated by Heigold et al. U.S. Patent 4,172,731. The particles can be process-soluble, as illustrated by Jelley et al. U.S. Patent 2,992,101, Hutton U.S. Patent 3,767,448, Naito U.S. Patent 4,094,848, Vallarino et al. U.S. Patent 4,447,525, Himmelmann et al. U.S. Patent 4,524,131 and Japanese Patent Applications 62/14467 and 61/230136. The matte can be resistant to removal in the process, as illustrated by Ishii U.S. Patent 4,396,706. The particles can be alkali-swellable but not removable, as illustrated by Bruck et al. U.S. Patent 4,301,240. Combinations of process-insoluble and process-soluble matting agents can be used.

(4) Relatively recently published examples of matting agents are provided by Podszun et al. U.S. Patent 5,093,445, Fautz U.S. Patent 4,980,273, Vandenberghe et al. U.S. Patent 4,766,059, Grzeskowiak et al. U.S. Patent 4,711,838, Lalvani et al. U.S. Patent 4,940,653, Katoh et al. U.S. Patent 4,952,484, Okamura et al. U.S. Patent 5,057,407, Ogasawara et al. U.S. Patent 5,204,233, Ishigaki et al. U.S. Patent 5,206,127, Nitschke et al. U.S. Patent 4,997,735, Ishigaki U.S. Patent 5,122,445, Arai et al. U.S. Patent 5,070,005, Nishio et al. U.S. Patent 5,252,448, Elton et al. U.S. Patent 5,104,914, Sterman et al. U.S. Patent 5,288,598, Sterman et al. U.S. Patent 5,300,411, Takada U.S. Patent 5,352,569, Tashiro



et al U.S. Patent 5,370,982, Smith et al U.S. Patent 5,378,577, Yamashita et al U.S. Patent 5,380,637, Waterman U.S. Patent 5,415,969, Jury U.S. Patent, 5,420,006, Fornasari et al U.S. Patent 5,441,860, Kanetake et al EPO 0 567 118, Baldassarri et al EPO 0 479 029, Besio et al EPO 0 370 405, Haga et al EPO 0 350 022, Harris EPO 0 341 200, Shor EPO 0 282 171, Lalvani et al EPO 0 262 504 and Bagchi EPO 0 307 855.

## X. Dye image formers and modifiers

The photographic elements can be color photographic elements which form dye images through the selective destruction, formation or physical removal of dyes.

### A. Silver dye bleach

The photographic elements can produce dye images through the selective destruction of dyes or dye precursors, such as silver-dye-bleach processes, as illustrated by A. Meyer, *The Journal of Photographic Science*, Vol. 13, 1965, pp. 90-97. Bleachable azo, azoxy, xanthene, azine, phenylmethane, nitroso complex, indigo, quinone, nitro-substituted, phthalocyanine and formazan dyes as illustrated by Stauner et al U.S. Patent 3,754,923, Piller et al U.S. Patent 3,749,576, Yoshida et al U.S. Patent 3,738,839, Froehlich et al U.S. Patent 3,716,368, Piller U.S. Patent 3,655,388, Williams et al U.S. Patent 3,642,482, Gilman U.S. Patent 3,567,448, Loeffel U.S. Patent 3,443,953, Anderau U.S. Patents 3,443,952 and 3,211,556, Mory et al U.S. Patents 3,202,511 and 3,178,291 and Anderau et al U.S. Patents 3,178,285 and 3,178,290, as well as their hydrazo, diazonium and tetrazolium precursors and leuco and shifted derivatives as illustrated by U.K. Patents 923,265, 999,996 and 1,042,300, Pelz et al U.S. Patent 3,684,513, Watanabe et al U.S. Patent 3,615,493, Wilson et al U.S. Patent 3,503,741, Boes et al U.S. Patent 3,340,059, Gompf et al U.S. Patent 3,493,372, Puschel et al U.S. Patent 3,561,970, Mowrey et al U.S. Patent 4,168,170, Marthaler et al U.S. Patent 4,304,846, Mollet et al U.S. Patent 4,374,914, Lenoir et al U.S. Patent 4,379,819 and Lenoir U.S. Patent 4,575,482 can be employed. More recent developments in dye bleach applications are shown in Ohlschlager et al U.S. 4,458,009, Schadt U.S. 4,460,679, Kriebel U.S. 4,704,349, Schellenberg U.S. 4,803,151, Kuhn U.S. 4,837,133, Baettig U.S. 5,043,257 and EPO 0 351 740.

### B. Image-dye-forming couplers

(1) The photographic elements can produce dye images through the selective formation of dyes such as by reacting (coupling) a color-developing agent (e.g., a primary aromatic amine) in its oxidized form with a dye-forming coupler. In one form, the dye-forming couplers are chosen to form subtractive primary (i.e., yellow, magenta and cyan) image dyes and are nondiffusible, colorless couplers, such as 2- and 4-equivalent couplers of the open-chain ketomethylene, pyrazolone,

pyrazolotriazole, pyrazolobenzimidazole, phenol and naphthol type, hydrophobically ballasted for incorporation in high-boiling organic (coupler) solvents. Such couplers are illustrated by Salminen et al U.S. Patents 2,423,730, 2,772,162, 2,895,826, 2,710,803, 2,407,207, 3,737,316 and 2,367,531, Loria et al U.S. Patents 2,772,161, 2,600,788, 3,006,759, 3,214,437 and 3,253,924, McCrossen et al U.S. Patent 2,875,057, Bush et al U.S. Patent 2,908,573, Gledhill et al U.S. Patent 3,034,892, Weissberger et al U.S. Patents 2,474,293, 2,407,210, 3,062,653, 3,265,506 and 3,384,657, Porter et al U.S. Patent 2,343,703, Greenhalgh et al U.S. Patent 3,127,269, Feniak et al U.S. Patents 2,865,748, 2,933,391 and 2,865,751, Bailey et al U.S. Patent 3,725,067, Beavers et al U.S. Patent 3,758,308, Lau U.S. Patent 3,779,763, Fernandez U.S. Patent 3,795,829, U.K. Patent 969,921, U.K. Patent 1,241,069, U.K. Patent 1,011,940, VandenEynde et al U.S. Patent 3,762,921, Beavers U.S. Patent 2,983,608, Loria U.S. Patents 3,311,476, 3,408,194, 3,458,315, 3,447,928 and 3,476,563, Cressman et al U.S. Patent 3,419,390, Young U.S. Patent 3,419,391, Lestina U.S. Patent 3,519,429, U.K. Patent 975,928, U.K. Patent 1,111,554, Jaeken U.S. Patent 3,222,176 and Canadian Patent 726,651, Schulte et al U.K. Patent 1,248,924, Whitmore et al U.S. Patent 3,227,550, Lau U.S. Patent 4,333,999, Lestina U.S. Patent 4,443,536, Booms et al U.S. Patent 4,420,556 (controlled smearing), Lau U.S. Patent 4,401,752, Bowne et al EPO 0 284 239, Kilminster et al EPO 0 271 323, Kilminster et al EPO 0 271 324, Romanet et al EPO 0 285 274, Bowne et al EPO 0 284 240, Krishnamurthy WO 88/04795, Kilminster et al U.S. Patent 4,753,871 and Bailey et al U.S. Patent 4,728,598. Polymeric couplers are also useful, as described by, for example, Tang et al U.S. Patent 4,804,260, Sato et al U.S. Patent 4,540,654 and Hirano et al U.S. Patent 4,576,910.

(2) Further types of image dye forming couplers are taught in Mooberry et al U.S. Patent 4,840,884, Harder U.S. Patent 4,948,722, Kaneko U.S. Patent 4,970,142, Moore U.S. Patent 4,973,545, Kobayashi et al U.S. Patent 5,017,466, Kawagishi et al 5,021,329, Kita et al U.S. Patent 5,024,930, Lestina et al U.S. Patent 5,051,343, Lau et al U.S. Patent 5,091,291, Crawley et al U.S. Patent 5,143,821, Sato et al U.S. Patent 5,162,156, Shinada et al U.S. Patent 5,164,289, Katoh et al U.S. Patent 5,169,749, Sato et al U.S. Patent 5,206,129, Mooberry et al U.S. Patent 5,246,820, Fujita et al U.S. Patent 5,296,339, Krishnamurthy U.S. Patent 5,306,604, Krishnamurthy U.S. Patent 5,318,884, Tang et al U.S. Patent 5,340,708, Tang et al U.S. Patent 5,358,836, Tang et al U.S. Patent 5,358,837, Chen et al U.S. Patent 5,360,710, Krishnamurthy et al U.S. Patent 5,399,467, Naoki et al EPO 0 500 043, Lau et al EPO 0 523 641, Masumi et al EPO 0 531 906, Crawley et al WO 92/00299, Hubsch et al DE 4,243,784 and Bergthaller DO 4,016,418.

(3) Polymeric type couplers are disclosed in Tang et al U.S. Patent 4,804,620, Yamanouchi et al U.S. Patent 4,874,689,

Sato et al U.S. Patent 4,877,720, Helling U.S. Patent 4,921,782, Maekawa et al U.S. Patent 4,946,771, Sakanoue et al U.S. Patent 4,960,688, Tang et al U.S. Patent 4,992,359, Cause et al U.S. Patent 5,017,667, Hirano et al U.S. Patent 5,055,386, Lau U.S. Patent 5,141,844, Sakanoue et al U.S. Patent 5,151,356, Takahashi et al U.S. Patent 5,169,742, Hirano et al EPO 0 283 938 and Yamanouchi et al EPO 0 316 955.

(4) Couplers which combine with oxidized developer to produce cyan colored dyes are shown, for example, in Weissberger et al U.S. Patent 2,474,293, Vittum et al U.S. Patent 3,002,836, Stecker U.S. Patent 3,041,236, Ono et al U.S. Patent 4,746,602, Kilminster U.S. Patent 4,753,871, Aoki et al U.S. Patent 4,770,988, Kilminster et al U.S. Patent 4,775,616, Hamada et al U.S. Patent 4,818,667, Masukawa et al U.S. Patent 4,818,672, Monbaliu et al U.S. Patent 4,822,729, Monbaliu et al U.S. Patent 4,839,267, Masukawa et al U.S. Patent 4,840,883, Hoke et al U.S. Patent 4,849,328, Miura et al U.S. Patent 4,865,961, Tachibana et al U.S. Patent 4,873,183, Shimada et al U.S. Patent 4,883,746, Tani et al U.S. Patent 4,900,656, Ono et al U.S. Patent 4,904,575, Tachibana et al U.S. Patent 4,916,051, Nakayama et al U.S. Patent 4,921,783, Merkel et al U.S. Patent 4,923,791, Tachibana et al U.S. Patent 4,950,585, Aoki et al U.S. Patent 4,971,898, Lau U.S. Patent 4,990,436, Masukawa et al U.S. Patent 4,996,139, Merkel U.S. Patent 5,008,180, Wolff U.S. Patent 5,015,565, Tachibana et al U.S. Patent 5,011,765, Kida et al U.S. Patent 5,011,766, Masukawa et al U.S. Patent 5,017,467, Hoke U.S. Patent 5,045,442, Uchida et al U.S. Patent 5,051,347, Kaneko U.S. Patent 5,061,613, Kita et al U.S. Patent 5,071,737, Langen et al U.S. Patent 5,075,207, Fukunada et al U.S. Patent 5,091,297, Tsukahara et al U.S. Patent 5,094,938, Shimada et al U.S. Patent 5,104,783, Fujita et al U.S. Patent 5,178,993, Naito et al U.S. Patent 5,813,729, Ikesu et al U.S. Patent 5,187,057, Tsukahara et al U.S. Patent 5,192,651, Schumann et al U.S. Patent 5,200,305, Yamakawa et al U.S. Patent 5,202,224, Shimada et al U.S. Patent 5,206,130, Ikesu et al U.S. Patent 5,208,141, Tsukahara et al U.S. Patent 5,210,011, Sato et al U.S. Patent 5,215,871, Kita et al U.S. Patent 5,223,386, Sato et al U.S. Patent 5,227,287, Suzuki et al U.S. Patent 5,256,526, Kobayashi et al U.S. Patent 5,258,270, Shimada et al U.S. Patent 5,272,051, Ikesu et al U.S. Patent 5,306,610, Yamakawa U.S. Patent 5,326,682, Shimada et al U.S. Patent 5,366,856, Naruse et al U.S. Patent 5,378,596, Takizawa et al U.S. Patent 5,380,638, Lau et al U.S. Patent 5,382,502, Matsuo et al U.S. Patent 5,384,236, Takada et al U.S. Patent 5,397,691, Kaneko et al U.S. Patent 5,415,990, Asami U.S. Patent 5,434,034, Tang et al U.S. Patent 5,441,863, Tashiro et al EPO 0 246 616, Lau EPO 0 250 201, Kilminster et al EPO 0 271 323, Sakanoue et al EPO 0 295 632, Mihayashi et al EPO 0 307 927, Ono et al EPO 0 333 185, Shima et al EPO 0 378 898, Glusto EPO 0 389 817, Sato et al EPO 0 487 111, Suzuki et al EPO 0 488 248, Ikesu et al EPO 0 539 034, Suzuki et al EPO 0 545 300,

Yamakawa et al EPO 0 556 700, Shimada et al EPO 0 556 777, Kawai EPO 0 556 858, Yoshioka EPO 0 569 979, Ikesu et al EPO 0 608 133, Merkel et al EPO 0 636 936, Merkel et al EPO 0 651 286, Sugita et al EPO 0 690 344, Renner et al German OLS 4,026,903, Langen et al German OLS 3,624,777 and Wolff et al German OLS 3,823,049.

(5) Magenta coupler types are shown, for example, in Porter et al U.S. Patents 2,311,082 and 2,369,489, Tuile U.S. Patent 3,152,896, Arai et al U.S. Patent 3,935,015, Renner U.S. Patent 4,745,052, Ogawa et al U.S. Patent 4,762,775, Kida et al U.S. Patent 4,791,052, Wolff et al U.S. Patent 4,812,576, Wolff et al U.S. Patent 4,835,094, Abe et al U.S. Patent 4,840,877, Wolff U.S. Patent 4,845,022, Krishnamurthy et al U.S. Patent 4,853,319, Renner U.S. Patent 4,868,099, Helling et al U.S. Patent 4,865,960, Normandin U.S. Patent 4,871,652, Buckland U.S. Patent 4,876,182, Bowne et al U.S. Patent 4,892,805, Crawley et al U.S. Patent 4,900,657, Furutachi U.S. Patent 4,910,124, Ikesu et al U.S. Patent 4,914,013, Yokoyama et al U.S. Patent 4,921,968, Furutachi et al U.S. Patent 4,929,540, Kim et al U.S. Patent 4,933,465, Renner U.S. Patent 4,942,116, Normandin et al U.S. Patent 4,942,117, Normandin et al U.S. Patent 4,942,118, Normandin et al U.S. Patent 4,959,480, Shimazaki et al U.S. Patent 4,968,594, Ishige et al U.S. Patent 4,988,614, Bowne et al U.S. Patent 4,992,361, Renner et al U.S. Patent 5,002,864, Burns et al U.S. Patent 5,021,325, Sato et al U.S. Patent 5,066,575, Morigaki et al U.S. Patent 5,068,171, Ohya et al U.S. Patent 5,071,739, Chen et al U.S. Patent 5,100,772, Harder et al U.S. Patent 5,110,942, Kimura et al U.S. Patent 5,116,990, Yokoyama et al U.S. Patent 5,118,812, Kunitz et al U.S. Patent 5,134,059, Mizukawa et al U.S. Patent 5,155,016, Romanet et al U.S. Patent 5,183,728, Tang et al U.S. Patent 5,234,805, Sato et al U.S. Patent 5,235,058, Krishnamurthy et al U.S. Patent 5,250,400, Ikenoue et al U.S. Patent 5,254,446, Krishnamurthy et al U.S. Patent 5,262,292, Matsuo et al U.S. Patent 5,300,407, Romanet et al U.S. Patent 5,302,496, Daifuku et al U.S. Patent 5,336,593, Singer et al U.S. Patent 5,350,667, Tang U.S. Patent 5,395,968, Helling et al U.S. Patent 5,354,826, Tang et al U.S. Patent 5,358,829, Ishidai et al U.S. Patent 5,368,998, Krishnamurthy et al U.S. Patent 5,378,587, Mizukawa et al U.S. Patent 5,409,808, Signer et al U.S. Patent 5,411,841, Wolff U.S. Patent 5,418,123, Tang U.S. Patent 5,424,179, Numata et al EPO 0 257 854, Bowne et al EPO 0 284 240, Webb et al EPO 0 341 204, Miura et al EPO 0 347,235, Yukio et al EPO 365,252, Yamazaki et al EPO 0 422 595, Kei EPO 0 428 899, Tadahisa et al EPO 0 428 902, Hiechi et al EPO 0 459 331, Sakanoue et al EPO 0 467 327, Kida et al, EPO 0 476 949, Kei et al, EPO 0 487 081, Wolfe EPO 0 489 333, Corallupi et al EPO 0 512 304, Hirabayashi et al EPO 0 515 128, Harabayashi et al EPO 0 534 703, Sato et al EPO 0 554 778, Tang et al EPO 0 558 145, Mizukawa et al EPO 0 571 959, Schofield et al EPO 0 583 832, Schofield et al EPO 0 583 834, Hirabayashi et al EPO 0 584 733, Tang et al EPO 0 602 748, Tang et al EPO

0 602 749, Lau et al EPO 0 605 918, Allway EPO 0 622 672, Allway EPO 0 622 673, Kita et al EPO 0 629 912, Kapp et al EPO 0 646 841, Kita et al EPO 0 656 561, Ishidai et al EPO 0 660 177, Tanaka et al EPO 0 686 872, Thomas et al WO 90/10253, Williamson et al WO 92/09010, Leyshon et al WO 92/10788, Crawley et al WO 92/12464, Williamson WO 93/01523, Merkel et al WO 93/02392, Krishnamurthy et al WO 93/02393, Williamson WO 93/07534, UK Patent Application 2,244,053, Japanese Patent Application 03192-350, Renner German OLS 3,624,103, Wolff et al German OLS 3,912,265, and Werner et al German OLS 40 08 067.

(6) Compounds useful for forming yellow colored dyes upon coupling with oxidized color developer include, for example, Weissberger U.S. Patent 2,298,443, Okumura et al U.S. Patent 4,022,620, Buckland et al U.S. Patent 4,758,501, Ogawa et al U.S. Patent 4,791,050, Buckland et al U.S. Patent 4,824,771, Sato et al U.S. Patent 4,824,773, Renner et al U.S. Patent 4,855,222, Tsoi U.S. Patent 4,978,605, Tsuruta et al U.S. Patent 4,992,360, Tomotake et al U.S. Patent 4,994,361, Leyshon et al U.S. Patent 5,021,333, Masukawa U.S. Patent 5,053,325, Kubota et al U.S. Patent 5,066,574, Ichijima et al U.S. Patent 5,066,576, Tomotake et al U.S. Patent 5,100,773, Lau et al U.S. Patent 5,118,599, Kuntz U.S. Patent 5,143,823, Kobayashi et al U.S. Patent 5,187,055, Crawley U.S. Patent 5,190,848, Motoki et al U.S. Patent 5,213,958, Tomotake et al U.S. Patent 5,215,877, Tsoi U.S. Patent 5,215,878, Hayashi U.S. Patent 5,217,857, Takada et al U.S. Patent 5,219,716, Ichijima et al U.S. Patent 5,238,803, Kobayashi et al U.S. Patent 5,283,166, Kobayashi et al U.S. Patent 5,294,531, Miyayashi et al U.S. Patent 5,306,609, Fukuzawa et al U.S. Patent 5,328,818, Yamamoto et al U.S. Patent 5,336,591, Saito et al U.S. Patent 5,338,654, Tang et al U.S. Patent 5,358,835, Tang et al U.S. Patent 5,358,838, Tang et al U.S. Patent 5,360,713, Morigaki et al U.S. Patent 5,362,617, Tosa et al U.S. Patent 5,382,506, Ling et al U.S. Patent 5,389,504, Tomotake et al U.S. Patent 5,399,474, Shibata U.S. Patent 5,405,737, Goddard et al U.S. Patent 5,411,848, Tang et al U.S. Patent 5,427,898, Himmelmann et al EPO 0 327 976, Clark et al EPO 0 296 793, Okusa et al EPO 0 365 282, Tsoi EPO 0 379 309, Kida et al EPO 0 415 375, Mader et al EPO 0 437 818, Kobayashi et al EPO 0 447 969, Chino et al EPO 0 542 463, Saito et al EPO 0 568 037, Tomotake et al EPO 0 568 196, Okumura et al EPO 0 568 777 and Yamada et al EPO 0 570 006, Kawai EPO 0 573 761, Carmack et al EPO 0 608 956, Carmack et al EPO 0 608 957, Mooberry et al EPO 0 628 865.

(7) The photographic elements can incorporate alkali-soluble ballasted couplers as illustrated by Froehlich et al and Tong, cited above. The photographic elements can be adapted to form nondiffusible image dyes using dye-forming couplers in developers as illustrated by U.K. Patent 478,984, Yager et al U.S. Patent 3,113,864, Vittum et al U.S. Patents 3,002,836, 2,271,238 and 2,362,598, Schwan et al U.S. Patent 2,950,970,

Carroll et al U.S. Patent 2,592,243, Porter et al U.S. Patents 2,343,703, 2,376,380 and 2,369,489, Spath U.K. Patent 886,723 and U.S. Patent 2,899,306, Tuile U.S. Patent 3,152,896 and Mannes et al U.S. Patents 2,115,394, 2,252,718 and 2,108,602.

(8) The photographic elements can produce dye images through selective removal of dyes. Negative or positive dye images can be produced by the immobilization or mobilization of incorporated color-providing substances as a function of exposure and development, as illustrated by U.K. Patents 1,456,413, 1,479,739, 1,475,265 and 1,471,752, Friedman U.S. Patent 2,543,691, Whitmore U.S. Patent 3,227,552, Bloom et al U.S. Patent 3,443,940, Morse U.S. Patent 3,549,364, Cook U.S. Patent 3,620,730, Danhauser U.S. Patent 3,730,718, Staples U.S. Patent 3,923,510, Oishi et al U.S. Patent 4,052,214 and Fleckenstein et al U.S. Patent 4,076,529.

(9) Image dye-forming couplers may be synthesized using processes such as those shown in Krishnamurthy et al U.S. 4,853,319, Arnold et al U.S. Patent 4,977,269, Crawley U.S. Patent 5,001,262, Kim et al U.S. Patent 5,055,586, Mizukawa U.S. Patent 5,214,149, Tang et al U.S. Patent 5,214,194, Tang et al U.S. Patent 5,237,030, Tang et al U.S. Patent 5,237,030, Crawley U.S. Patent 5,210,209, Begley et al U.S. Patent 5,239,081, Tang et al U.S. Patent 5,262,542, Tang U.S. Patent 5,276,158, Obayashi U.S. Patent 5,354,891, Krishnamurthy U.S. Patent 5,359,065, Takamine et al U.S. Patent 5,442,114, Huson et al EPO 0 430 335, Kimura et al EPO 0 473 464, Uchida et al EPO 0 495 313, Bergley et al EPO 0 520 498, Onda et al EPO 0 542,284, Bergthaller EPO 0 572,887, Yamakawa et al EPO 0 679 634, Mizukawa et al EPO 0 688 774, Pfeiffer et al East German DD 293,347, Solf et al German OLS 3,733,651, Bergthaller German OLS 4,040,472 and Mylroie WO 92/17455.

#### C. Image dye modifiers

(1) The photographic elements, in addition to comprising dye-forming couplers, can comprise image-modifying couplers or compounds. Such image-modifying couplers or compounds can contribute to dye density and can release, either directly or through one or more timing or linking groups, photographically useful fragments such as development accelerators (often referred to as fogging agents), development inhibitors, bleach accelerators, bleach inhibitors, developing agents (e.g. competing developing agents or auxiliary developing agents), silver complexing agents, fixing agents, toners, hardeners, tanning agents, anti-stain agents, stabilizers, antifoggants, desensitizers, and chemical or spectral sensitizers and compensating couplers. Release of the photographically useful fragments typically occurs upon reaction of the coupler or compound with oxidized developer, although it may also occur by other means, such as upon exposure to nucleophiles present in processing baths.

(2) Development accelerator releasing couplers (DARCs) are typically good reducing agents and often comprise a hydrazide group. They are exemplified in Inoue et al U.S. Patent 4,948,712, Twist et al EPO 0 364 280, Deguchi et al U.S. Patent 5,213,942, Yagihara et al U.S. Patent 5,132,201, Hirano et al EPO 0 303,301, and Matejcek et al U.S. Patent 4,820,616. Compounds previously believed to be development inhibitor releasing couplers or compounds, when used at sufficiently low levels in a photographic element, are now known to be effective as DARCs. Such are disclosed in Szajewski U.S. Patent 5,221,600.

(3) Bleach accelerators capable of being released from a bleach accelerator releasing coupler or compound (BARCs) often comprise the structure -S-L-X wherein L is a linking group and X is a hydrophilic group. Though not an exclusive list, the hydrophilic group can be a carboxy, morpholino, hydroxyl or substituted or unsubstituted amino group. BARCs are known to facilitate the oxidation of developed silver in bleach solutions. In certain instances, they may also enhance silver developability thereby affecting the contrast (gamma) of the emulsion in which they are contained. Known BARCs are exemplified in Matsushita U.S. Patents 4,966,835, 5,066,573, and 5,118,596, Michno et al U.S. Patent 4,912,024, Begley et al U.S. Patents 5,286,859, 5,318,879 and 5,358,824, Szajewski et al EPO 608,958, Asano EPO 0 383 623, Manthey et al EPO 0 518 101, Sakanoue et al EPO 0 310 125, EPO 0 301,477, U.S. Patents 5,063,145 and 4,842,994, and Hall et al EPO 0 193,389. In Szajewski U.S. Patent 5,135,839, Begley et al U.S. Patent 5,300,406, and Friday EPO 570 109 it is taught to combine BARCs with other image modifying couplers or compounds such as development inhibitor releasing compounds.

(4) Development inhibitor releasing couplers and compounds release development inhibitors directly (DIR) or through one or more links or timing groups (DIAR: development inhibitor anchimeric releasing). Development inhibitor releasing couplers and compounds can be used to perform such useful functions as gamma or curve shape control, sharpness enhancement, granularity reduction and color balance. They are exemplified in Whitmore et al U.S. Patent 3,148,062, Barr et al U.S. Patents 3,227,554 and 3,733,201, Sawdey U.S. Patent 3,617,291, Groet et al U.S. Patent 3,703,375, Abbott et al U.S. Patent 3,615,506, Weissberger et al U.S. Patent 3,265,506, Seymour U.S. Patent 3,620,745, Marx et al U.S. Patent 3,632,345, Mader et al U.S. Patent 3,869,291, U.K. Patent 1,201,110, Oishi et al U.S. Patent 3,642,485, Verbrughe U.K. Patent 1,236,767, Fujiwhara et al U.S. Patent 3,770,436, Matsuo et al U.S. Patent 3,808,945, Miyayashi et al U.S. Patent 5,429,917, Ishige et al EPO 0 529 992, which discloses specific yellow dye-forming DIR and DIAR couplers, Ohkawa et al EPO 0 438 148, Begley et al U.S. Patent 5,334,490 which discloses magenta dye-forming DIR and DIAR couplers, and EPO 0 436 338, Credner et al U.S. Patent 4,052,213, Fujiwhara

U.S. Patents 3,928,041 and 3,958,993, Inoue et al U.S. Patent 4,801,520, Berghaller et al German OLS 4,014,936, U.S. Patents 4,870,000 and 5,021,330, Odenwalder et al U.S. Patent 5,035,987, Shibahara et al U.S. Patent 4,952,485, Merkel et al EPO 655,648, EPO 651,288 and EPO 636,934, Begley et al EPO 594,256 and Ito et al EPO 0 384 671.

(5) Specific development inhibitor fragments include mercaptotetrazole derivatives, mercaptotriazole derivatives, mercaptimidazole derivatives, mercaptopyrimidine derivatives, mercaptobenzimidazole derivatives, mercaptothiadiazole derivatives, mercaptobenzothiazole derivatives, mercaptobenzoxazole derivatives, and indazole derivatives. They and the couplers or compounds that release them are illustrated in Matsushita et al U.S. Patent 5,116,717, and Delapato U.S. Patent 4,908,302, Lestina et al U.S. Patent 5,283,163 and Begley U.S. Patent 5,352,570. Ballasted development inhibitor fragments and the couplers or compounds that release them are disclosed in Szajewski et al U.S. Patent 4,962,018 and EPO 0 348 139, and Ohkawa et al U.S. Patent 4,938 150. Szajewski et al U.S. Patent 5,256,523 illustrates development inhibitor fragments comprising sterically hindered substituent groups. Development inhibitor fragments having thioether substituent groups are disclosed in Poslusny et al EPO 0 505 008 and Szajewski et al U.S. Patent 5,006,448. Triazole-type development inhibitor fragments are illustrated in Ohlschager et al U.S. Patent 4,840,880, Kunitz et al U.S. Patent 4,833,070, Odenwalder et al U.S. Patents 4,897,341, 5,200,306, EPO 0 272 573 and German OLS 3,736,048 and Vetter et al U.S. Patent 5,021,331. Such fragments are generally, but not exclusively, released from yellow dye forming couplers. Bucci U.S. Patent 5,006,452 and Begley et al EPO 0 540 118 disclose couplers capable of releasing benzotriazole-containing fragments that exhibit development inhibition properties. Development inhibitor fragments defined in terms of their diffusibility are exemplified in Yamada et al U.S. Patent 4,804,619 and Shimba et al EPO 0 507 092. Defining development inhibitor fragments in terms of their distribution coefficient between oil and water is disclosed in Bell et al DE 4,208,109. Development inhibitors useful in reversal photographic elements are disclosed in Hamer U.S. Patent 5,399,466, Harder U.S. Patent 5,411,839 and Berghaller et al DE 4,335,217.

(6) It has been recognized that many types of development inhibitor fragments released from DIR or DIAR couplers or compounds can diffuse out of photographic elements during processing and can accumulate in processing solutions, thus causing losses of speed in photographic materials subsequently processed in the solutions. One method to overcome this is to utilize development inhibitor fragments that are converted to inactive species in the developer solution. Use of these so-called "self-destruct" development inhibitors is disclosed in DeSelms U.S.

Patent 4,782,012, Sugita et al EPO 0 436 190 and EPO 0 440 466, Yasuhiro EPO 0 336 411, Miyayashi EPO 0 447 921, Ichijima U.S. Patent 4,477,563 and Vargas et al U.S. Patent 5,310,642.

(7) Development inhibitor releasing couplers and compounds can be incorporated into any of the layers of a photographic element. Incorporation into particular emulsions or elements having particular layer arrangements is illustrated in Simons U.S. Patent 4,857,448, Haraga et al U.S. Patent 5,051,345, Tamato et al EPO 0 318 992, Matejcek U.S. Patent 4,963,465, Pearce et al U.S. Patents 5,254,441, Twist et al U.S. Patent 5,264,335, Hall U.S. Patent 5,270,152, Murai U.S. Patent 5,399,471, Irie et al U.S. Patent 5,302,500, Szajewski et al WO 94/22054, Edwards U.S. Patent 5,372,920, Ford et al U.S. Patent 5,378,590, Ueda et al EPO 600,518, Bergthaller et al DE 4,418,511, and Hirabayashi et al EPO 0 365 348. Development inhibitor releasing couplers and compounds combined with specified dye-forming couplers or with other image modifying couplers or compounds are disclosed in Szajewski et al U.S. Patent 5,021,555, Taber U.S. Patent 4,980,267, Uchida et al U.S. Patent 5,385,814, Sowinski et al U.S. Patent 5,395,744, Merrill U.S. Patent 5,314,792, Begley et al EPO 577,183, Manthey et al U.S. Patent 5,288,594, Begley et al U.S. Patent 5,286,613, Bertoldi et al EPO 657,776, Baloga U.S. Patent 5,399,465, Miyayashi et al EPO 583,004, Ueda et al U.S. Patent 5,384,234, Miyayashi et al EPO 606,914, Harder U.S. Patent 5,380,633, Kimura et al EPO 0 296 785 and Yagi Japanese Application JA 63/74058.

(8) In addition to DIR and DIAR couplers, other compounds are known which are capable of releasing development inhibitor fragments. In particular, hydroquinone derivatives which undergo oxidation on development to release development inhibitor fragments are known. These compounds, which are generally referred to as DIR hydroquinones or inhibitor releasing developers (IRDs), can release photographically useful fragments other than development inhibitors, and are illustrated in Ono et al U.S. Patent 5,210,012, Nakamine et al U.S. Patent 5,202,225, Ichijima et al U.S. Patent 4,814,261 and EPO 0 281 118, Porter et al U.S. Patent 3,379,529, Barr et al U.S. Patent 3,364,022, Duennbier et al U.S. Patent 3,297,445, Rees et al U.S. Patent 3,287,129, Yagihara et al U.S. Patent 5,132,201, Kojima et al U.S. Patent 4,791,049, Stanley et al U.S. Patent 5,385,816, Ogawa et al EPO 0 513 496, Misui et al EPO 0 481 427, Hara et al EPO 0 537 659, and Nagaoka et al EPO 0 566 115. Compounds which oxidatively release photographically useful fragments from hydrazide compounds are described in Harder U.S. Patent 4,684,604.

(9) Couplers that are capable of releasing photographically useful fragments and of forming dyes that are washed out of the photographic element during processing are known. These couplers comprise a solubilizing group on the coupler parent and

typically a ballasting group on the coupling off group. Upon reaction with oxidized developer, the ballasted coupling off group is released from the coupler parent which can then be washed out of the photographic element. Exemplary couplers are illustrated in Begley et al U.S. Patents 5,151,343, 5,026,628, 5,234,800, 5,250,398, 5,239,081, 5,286,613, 5,286,859, 5,288,593, 5,264,582, 5,264,583, 5,272,043 and 5,279,929, EPO 0 522 371, EPO 0 525 396, EPO 0 576 087, EPO 0 577 183, EPO 0 577 191, EPO 0 577 193 and EPO 0 577 192, and Szajewski et al U.S. Patent 5,250,399. Nakagawa et al U.S. Patent 4,482,629 discloses naphtholic development inhibitor releasing couplers having a solubilizing group on the naphtholic moiety. Couplers that release photographically useful fragments and form dyes that are colorless are disclosed in Shimada EPO 0 346 899 and Fujiwara et al U.S. Patent 3,961,959.

(10) As noted, image modifying couplers and compounds can release photographically useful fragments via one or more linking or timing groups. Linking groups are generally those groups which decompose quickly to form small molecules such as carbon dioxide or formaldehyde. They are illustrated in Miyayashi et al EPO 0 517 214, Ohkawa et al EPO 0 438 129, and Obayashi EPO 0 514 896. Timing groups, by contrast, delay release of the photographically useful fragment and function, typically, by electron transfer down a conjugated chain or cyclization of reaction (nucleophilic displacement). Illustrative examples of such groups are disclosed in Begley et al U.S. Patents 4,857,440 and 5,021,322, and Manthey EPO 0 518 101. Heterocyclic timing groups are illustrated in Miyayashi EPO 0 499 279 and EPO 0 523 451, and Begley et al U.S. Patent 4,847,185. Image modifying couplers and compounds capable of releasing photographically useful fragments through multiple linking or timing groups are illustrated in Burns et al U.S. Patent 4,861,701, and Miyayashi EPO 0 529 436. Other linking and timing groups are described in Sato et al U.S. Patent 4,409,323, Lau U.S. Patent 4,248,962, Slusarek et al U.S. Patents 5,034,311, 5,055,384 and 5,262,291, Begley U.S. Patent 5,306,607 and EPO 0 514 896, Begley U.S. Patent 5,288,593, Ohkawa et al U.S. Patent 5,286,620, Begley et al EP 576,087 and EPO 576,089. Timing groups that require reaction with oxidized developer in order to release the photographically useful fragment are disclosed in, for example, Miyayashi et al EPO 0 435 334 and EPO 0 451 526, Ueda et al U.S. Patent 4,818,664, Abe et al U.S. Patent 4,873,179, Kume et al U.S. Patent 4,933,989, Ichijima et al U.S. Patent 5,071,735, Deguchi et al U.S. Patent 4,618,571, Katoh et al U.S. Patent 5,221,599, and Toyoda et al EPO 0 503 658. Image-modifying couplers capable of releasing multiple photographically useful fragments are disclosed in Motoki et al EPO 0 464 612.

(11) Blocked photographically useful fragments which release such fragments upon reaction with nucleophiles are illustrated in Buchanen et al U.S. Patents 5,019,492, 5,242,783,

and EPO 0 547 707 in which blocked photographically useful fragments are disclosed which deblock in the presence of peroxides, Matsushita U.S. Patent 5,116,717, Nielson et al U.S. Patent 5,233,581, Okada et al U.S. Patent 5,204,213, Yagihara U.S. Patent 4,659,651, and Ono et al U.S. Patent 4,734,353. Blocked photographically useful fragments which release such fragments upon reduction are illustrated in Katoh U.S. Patent 5,064,752. Other blocked fragments are described in Kapp et al U.S. Patent 5,283,162.

(12) The photographically elements may contain couplers or compounds that release other types of photographically useful fragments. Couplers or compounds that release fluorescent groups are exemplified in Sato et al U.S. Patent 5,204,232, Tanaka et al U.S. Patent 5,236,804, and Ravindran et al U.S. Patent 4,774,181. Couplers or compounds that release fragments that scavenge oxidized developer during processing are illustrated in Watanabe et al U.S. Patent 5,084,373, Sakanoue et al U.S. Patent 5,272,049, Masukawa et al EPO 0 297 836, Okusa et al EPO 0 383 637, and Kimura et al U.S. Patent 5,128,237. Couplers or compounds that release electron transfer agents are as described in Platt et al U.S. Patent 4,912,025, and Michno et al U.S. Patent 4,859,578. Compounds that release water soluble transition metal complexes having discoloration inhibition effects are disclosed in Koya U.S. Patent 5,071,729. Compounds capable of releasing nucleating agents are illustrated in EPO 0 399 460. Compounds capable of releasing silver halide color developers or precursors thereof are disclosed in U.S. Patent 5,240,821. Compounds capable of releasing a coupler with an adhering group with an affinity for silver are described in Odenwälder et al U.S. Patent 5,441,857.

#### D. Hue modifiers/stabilization

(1) Compounds used to modify the hue produced by an image dye can include those such as the amine compounds with electron attractive groups described in Sato et al U.S. patent 5,019,493.

(2) The photographic elements can contain antistain agents (i.e., oxidized developing-agent scavengers) to prevent developing agents oxidized in one dye image layer unit from migrating to an adjacent dye image layer unit. Such antistain agents include ballasted or otherwise nondiffusing antioxidants as illustrated by Weissberger et al U.S. Patent 2,336,327, Loria et al U.S. Patent 2,728,659, Vittum et al U.S. Patent 2,360,290, Jelley et al U.S. Patent 2,403,721 and Thirtle et al U.S. Patent 2,701,197. To avoid auto-oxidation, the antistain agents can be employed in combination with other antioxidants as illustrated by Knechel et al U.S. Patent 3,700,453. Another example of an oxidized developing-agent scavenger is described by Ross et al U.S. Patent 4,447,523 (2,4-disulfonamidophenols). Further antistain agents include the following: Tanji et al U.S. Patent 4,945,034 (pyrazolotriazoles and quenchers of particular reactive

ities), Morigaki et al U.S. Patent 5,047,315 (antistain agents plus particular solvents), Aoki et al U.S. Patent 5,096,805 (5-pyrazolones with amines to prevent stain), Morigaki et al U.S. 5,108,876 (phenylsulfoxyls), Morigaki et al U.S. Patent 5,176,989 (coupler solvent dispersions containing polymer and antistain compound), Morigaki et al U.S. 5,194,348 (various esters of specified reaction rate constants), Mihayashi et al EPO 0 250 723 (amido bis-phenols), Mihayashi et al EPO 0 267 618 (carbamoyl or sulfamoyl substituted hydroquinones), Nakamura et al EPO 0 284 099 (reducing groups linked to oxidized developer coupling groups), Nelson et al EPO 0 459 340 (hydrazides), Morigaki et al EPO 0 544 317 (pyrazolotriazole cyan couplers and various lipophilic compounds) and Merkel et al EPO 0 545 248 (protic imidazole or a pyridine with 2-equivalent pyrazolone magenta couplers). Further developments in the use of oxidized developer scavengers in photographic elements are found in the following: Harder U.S. Patent 4,923,787, Henzel et al U.S. Patent 4,927,744, Takahashi U.S. Patents 5,021,328 and 5,082,764, Zengerle et al U.S. Patent 5,360,702, Merkel et al EPO 0 658 806, Sakai EPO 0 384 487, Nakatsugawa et al EPO 0 516 065, Sibuya et al EPO 0 520 310, Singer et al EPO 0 654 702 and Schmuck et al DE 41 40 946.

(3) The photographic elements can include image-dye stabilizers. Such image-dye stabilizers are illustrated by U.K. Patent 1,326,889, Lestina et al U.S. Patents 3,432,300 and 3,698,909, Stern et al U.S. Patent 3,574,627, Brannock et al U.S. Patent 3,573,050, Arai et al U.S. Patent 3,764,337 and Smith et al U.S. Patent 4,042,394. Further dye stabilizers include the phenols and blocked phenols (that is, with an H of the alcohol group replaced with some other substituent) described in Ohbayashi et al U.S. Patent 4,745,049 (yellow couplers and phenols blocked with carbamoyl groups), Morigaki et al U.S. Patent 4,929,538 (naphtholic coupler with blocked phenols or N-containing heterocycles), Rody et al U.S. Patent 5,006,665 (phenolic thianes), Leppard U.S. Patent 5,059,515 (blocked phenols), Mizukura et al U.S. Patent 5,071,738 (phenol polymers), Leppard et al U.S. Patent 5,145,766 (magenta couplers with carboxyl substituted phenols), Leppard et al EPO 0 415 883 (phenols and bis-phenols), Seto et al EPO 0 544 316 (blocked phenol or anilines and pyrazolazole couplers), Hagemann et al EPO 0 563 638 (pyrazolazole magenta couplers plus urea substituted phenols) and Stanley et al WO 91/18323. Further dye stabilizers are shown in: Kita et al U.S. Patent 5,376,520 and Seto et al U.S. Patent 5,278,039, Ohki et al U.S. Patent 5,397,689, Leppard et al U.S. Patent 5,411,847, Wolff et al U.S. Patent 5,415,989, Hagemann U.S. Patent 5,426,022, Jain et al U.S. Patent 5,434,041.

(4) Hydroquinone and blocked hydroquinone stabilizers are described in Liebe et al U.S. Patent 4,755,452 (magenta couplers plus hydroquinones and indoles), Ohki et al U.S. Patent



4,988,613 (bis-hydroquinones), Seto et al U.S. Patent 5,004,678, Abe et al U.S. Patent 5,063,131 (phenylcarbamoyl substituted hydroquinones), Mitsui et al U.S. Patent 5,079,133, Abe et al U.S. Patent 5,153,109 (carbamoyl or sulfamoyl substituted hydroquinones), Nishijima U.S. Patent 5,208,140, Otani et al EPO 0 481 333 (sulfo substituted hydroquinones), Yamazaki et al EPO 0 520 726 (yellow couplers and blocked hydroquinones), Leppard et al Takahashi EPO 0 573 008, Weinmann et al. EPO 0 585 546, Leppard et al. EPO 0 586 343, German OLS 4,008,785 (pyrazoloazole magenta couplers and blocked hydroquinones) and Leppard et al German OLS 4,012,305 (pyrazolone magenta couplers and blocked hydroquinones).

(5) Bisphenol and blocked bisphenol stabilizers are described in Goddard et al U.S. Patents 4,749,645 (bis-phenols blocked with phosphates) and 4,782,011 (blocked bis-phenols), Goddard U.S. Patents 4,794,072 (bis-phenylphosphates) and 4,980,275 (bis-phenols blocked with phosphate groups), Idogaki U.S. Patent 5,108,886 (pyrazoloazole magenta couplers dispersed in chlorinated paraffins, with bisphenols), Sugita et al U.S. Patent 5,063,148, Idogaki et al. U.S. Patent 5,294,529, Seto et al U.S. Patent 5,294,530, Krishnamurthy et al. U.S. Patent 5,426,021, Hagenmann et al. U.S. Patent 5,436,125, Jain et al U.S. Patent 5,437,962, Weber et al. U.S. Patent 5,441,855, Weber et al U.S. Patent 5,441,861, Weber et al U.S. Patent 5,441,862, Weber et al DE 4,307,4439 and Leyshon et al WO 91/08515.

(6) Stabilizers with spiro type structures are described in Seto et al U.S. Patent 4,864,039 (spirobenzofurans antioxidants), Morigaki et al U.S. Patent 4,868,101 and Seto et al U.S. Patent 4,895,793 (spiroindanes), Shono U.S. Patent 5,332,655.

(7) Stabilizers with other heterocyclic structures are described in Sugita et al U.S. Patent 4,814,262 (phenoxy compounds with pyrrolidone, piperidine, morpholine or pyridine substituents, particularly for pyrazoloazole couplers), Kaneko U.S. Patent 4,880,733 (pyrazoloazoles with thiomorpholines), Kaneko et al U.S. Patent 4,973,546 (pyrazoloazoles with morpholines, thiomorpholines, chromans, coumarans, and indanes), Furutachi et al U.S. Patent 5,001,045 (yellow couplers and epoxides), Nishijima U.S. Patent 5,017,465 (pyrazoloazoles with phenoxy compounds having heterocyclic nitrogen substituents), Morigaki U.S. Patent 5,028,519 (various nitrogen heterocyclic compounds), Nishijima et al U.S. Patent 5,082,766, Nishijima et al U.S. Patent 5,091,294, Takahashi et al U.S. Patent 5,120,636, Takahashi et al U.S. Patent 5,183,731 (yellow couplers and epoxides), Seto et al U.S. Patent 5,190,853 (hydrazide or cyclic azo stabilizers), Negoro et al U.S. Patent 5,360,711, Takizawa et al U.S. Patent 5,378,595, Seto et al U.S. Patent 5,411,846, Deguchi et al U.S. Patent 5,415,982, Yoshioka et al U.S. Patent 5,418,121, Seto U.S. Patent 5,429,918, Jain et al U.S. Patent 5,434,040, Kaneko EPO 0 286 850, Naruse et al EPO 0 319 985

(pyrazolotriazoles plus heterocyclic nitrogen compounds), Tomiyama et al EPO 0 472 153 (epoxides), Shono et al EPO 0 508 398 (acylacetamide yellow couplers with phenols or heterocyclic stabilizers), Deguchi EPO 0 543 367 (pyrazoloazole couplers with epoxides), Edwards et al EPO 0 570 975, Chari et al WO 94/16363 and Leyshon et al WO 91/11749 (chromanols).

(8) Stabilizers of organometallic complexes are described in Suzuki U.S. Patent 4,904,574 (Ni complexes), Suzuki U.S. Patent 4,981,773 (Ni complexes), Sugita et al U.S. Patent 4,931,383 (pyrazoloazoles with organometallic complexes), Nishijima et al U.S. Patent 5,017,464 (pyrazoloazole couplers plus Ni complexes, phenols and/or piperidines), Sobel et al German OLS 4,110,487 (Ni complexes as stabilizers).

(9) Other types of stabilizers are described in Krishnamurthy U.S. Patent 4,740,438 (phenyl disulfides), Mihayashi et al U.S. Patent 4,904,579 (pyrazolone magenta coupler with diffusion resistant carboxylic acid compounds), Seto et al U.S. Patent 4,910,126 (pyrazolotriazoles with phosphates), Lau et al U.S. Patent 4,914,005 (cyan couplers and alkoxyacrylate polymer latexes), Rody et al U.S. Patent 4,933,271 (thiopyrans), Morigaki et al U.S. Patent 4,939,072 (phenylsulfonfyls), Nishijima et al U.S. Patent 4,959,300 (pyrazoloazole couplers with surfactants having carboxylic sulfonic or sulfuric ester groups), Morigaki et al U.S. Patent 4,994,359 (5-pyrazolone magenta couplers with tertiary amines having carboxyl, amide or phosphate substituents), Aoki et al U.S. Patent 5,009,989 (aliphatic esters with cyan phenolic couplers), Nakamura et al U.S. Patent 5,035,988 (yellow couplers and various stabilizers), Rody et al U.S. Patent 5,059,689 (triazines), Bowne U.S. Patent 5,147,764, Aoki et al U.S. Patent 5,162,197 (phenolic couplers plus esters), Bagchi et al U.S. Patent 5,185,230 (coupler containing dispersed droplets surrounded by polyvinyl alcohol layer), Seto et al U.S. Patent 5,192,650 (boron compounds), Merkel et al U.S. Patent 5,200,309 (2-equivalent pyrazolone couplers plus carbonamide, aniline or amine compounds to reduce continued coupling), Merkel et al U.S. Patent 5,232,821 (magenta couplers and sulfone or sulfoxides), Takashi et al U.S. Patent 5,288,599, Deguchi U.S. Patent 5,294,527, Furutachi U.S. Patent 5,294,528, Seto et al U.S. Patent 5,300,419, Sato U.S. Patent 5,304,463, Yoshioka et al U.S. Patent 5,314,797, Shono et al U.S. Patent 5,324,626, Negoro et al U.S. Patent 5,395,749, Yoshioka U.S. Patent 5,397,688, Shono et al U.S. Patent 5,399,473, Yoshioka et al U.S. Patent 5,403,704, Yoshioka et al U.S. Patent 5,409,807, Seto U.S. Patent 5,418,122, Chari U.S. Patent 5,426,019, Jain et al U.S. Patent 5,436,124, Janssens et al EPO 0 312 657 (alkali labile couplers), Ootaguro et al EPO 0 403 797 (arylnitroso compounds or aryl hydrazyls), Nishimura et al EPO 0 486 216 (stabilizers of specified singlet oxygen quenching ability), Merkel et al EPO 0 510 576 (pyrazolone magenta dye forming couplers plus sulfide compounds to reduce continued coupling), Nishimura et al EPO



0 520 412 (esters with specified oxidation potentials), Seto et al EPO 0 524 540 (yellow couplers with amide, phosphorous or hydrazine compounds), Suzuki et al EPO 0 544 323 (pyrazolotriazole cyan couplers sparingly water soluble polymers) and Morigaki et al EPO 0 545 305 (pyrazolotriazole cyan couplers with lipophilic phenol, sulfur peroxide or amide compounds), Nishijima et al EPO 0 585 679, Takizawa et al EPO 0 606 659, Bagchi et al EPO 0 609 878 (oxygen barrier coated milled dispersion particles).

(10) Particular types of solvents used to increase the stability of dyes formed from various couplers are described in Kobayashi et al U.S. Patent 4,923,783 (cyan dye former with aryl carboxylate high boiling solvents), Nishijima U.S. Patent 4,954,432 (yellow couplers with solvents of specified dielectric constants), Shimura et al U.S. Patent 5,238,790 (aromatic ester or aromatic amide solvent), Takahashi et al U.S. Patent 5,242,788 (pyrazolotriazoles and aliphatic ester solvents), Merkel et al U.S. Patent 5,258,278 (carbonamide compounds with pyrazolotriazole magenta couplers), Takahashi U.S. Patent 5,370,978 (pyrazolotriazole cyan coupler with carboxylic acid ester solvent), Nakagawa et al U.S. Patent 5,376,512 (epoxy and amide solvents with yellow couplers), Merkel et al U.S. Patent 5,378,593 (carbonamide solvents with 2-phenylcarbamoyl-1-naphthol DIR and DIAR couplers), Sugita et al U.S. Patent 5,382,500 (sulfonamide or phenolic solvents with magenta couplers), Weber et al U.S. Patent 5,508,157 (N,N-hydroxyalkyl substituted ureas with pyrazolotriazole magenta couplers), Sasaki et al EPO 0 271 005 (solvents of particular dielectric constants with cyan phenolic couplers), Young EPO 0 533 964 (solvents having particular melting points), Takahashi et al EPO 0 560 198 (pyrazolotriazole solvents with high molecular weight compounds, preferably phenols, and solvents of particular dielectric constant), Merkel et al EPO 0 570 973 (phenolic solvents with 2-phenylcarbamoyl-1-naphthol DIR and DIAR couplers), Kita et al EPO 0 692 737 (monohydric alcohols primarily with pyrazolotriazole magenta couplers), Weber et al German DE 43 43 194 (polyol ester solvents, primarily with pyrazolotriazole magenta couplers).

(11) Combinations of various stabilizers are described in Ohbayashi et al U.S. Patent 4,797,350 (blocked phenols and piperidines), Takada et al U.S. Patent 4,820,614, Komorita et al U.S. Patent 4,863,840 (stabilizers plus solvents of particular dielectric constants), Hirabayashi et al U.S. Patent 4,882,267 (phosphates plus sulfamoyls), Ishikawa et al U.S. Patent 5,006,438, Sasaki et al U.S. Patent 5,006,454 (pyrazolotriazole magenta coupler, plus hydroquinone and compound of specified oxidation potential), Aoki U.S. Patent 5,037,730 (phenolic cyan couplers plus epoxides), Patent 5,049,482 (blocked hydroquinones), Seto et al U.S. Patent 5,068,172, Furutachi et al U.S. Patent 5,098,805, Seto et al U.S. Patent 5,104,781 (pyrazolotriazoles with N-heterocycles or phenols, and phosphates), Seto et al U.S. Patent 5,104,782 (bisphenols plus phenols), Seto et

et al U.S. Patent 5,139,931 (pyrazolotriazoles with phosphates and phenols), Matsumoto et al U.S. Patent 5,156,945, Yoneyama et al U.S. Patent 5,200,304 (phenolic cyan couplers with quinones or hydroquinones and epoxides), Morigaki et al U.S. Patent 5,212,055 (pyrazolotriazole couplers plus spiroindanes and bisphenols), Kadokura et al U.S. Patent 5,236,819, Morigaki et al U.S. Patent 5,242,785 (ethers, thioethers or amines with other compounds), Takahashi et al U.S. Patent H706 (sulfo and sulfone compounds), Nishijima et al U.S. Patent 5,132,202, Hagemann et al U.S. Patent 5,362,615, Takada et al German OLS 3,902,676 (hydroquinones, benzotriazoles and amines in various combinations), Yoneyama EPO 0 538 862 (yellow couplers, bisphenols and epoxides).

#### E. Dispersing dyes and dye precursors

Dyes and dye precursors, typically dye-forming couplers, can be incorporated in the photographic elements as illustrated by Schneider et al, *Die Chemie*, Vol. 57, 1944, p. 113, Mannes et al U.S. Patent 2,304,940, Martinez U.S. Patent 2,269,158, Jelliey et al U.S. Patent 2,322,027, Froehlich et al U.S. Patent 2,376,679, Fierke et al U.S. Patent 2,801,171, Smith U.S. Patent 3,748,141, Tong U.S. Patent 2,772,163, Thirtle et al U.S. Patent 2,835,579, Sawdey et al U.S. Patent 2,533,514, Peterson U.S. Patent 2,353,754, Seidel U.S. Patent 3,409,435 and Chen Research Disclosure, Vol. 159, July, 1977, Item 15930.

Further developments in the art of incorporating couplers into photographic elements are found in the following: Takada et al U.S. Patent 4,753,870, Takahashi et al U.S. Patent 4,797,349, Baldassarri et al U.S. Patent 4,822,724, Lolocono et al U.S. Patent 4,822,728, Okumura et al U.S. Patent 4,830,958, Ogawa et al U.S. Patent 4,857,449, Delprato et al U.S. Patent 4,873,182, Ozawa et al U.S. Patent 4,874,688, Zengerle U.S. Patent 4,885,234, Wolff et al U.S. Patent 4,898,811, Leemans et al U.S. Patent 4,908,155, Sasaki et al U.S. Patent 4,910,127, Nishijima et al U.S. Patent 4,916,050, Bagchi U.S. Patents 4,933,270 and 4,970,139, Takahashi et al U.S. Patent 4,946,770, Renner et al U.S. Patent 4,952,487, Chari U.S. Patent 4,957,857, Terai et al U.S. Patent 4,987,062, Delprato et al U.S. Patent 5,013,639, Bagchi et al U.S. Patent 5,013,640, Yoneyama U.S. Patent 5,026,631, Junkers et al U.S. Patent 5,043,255, Sakai et al U.S. Patent 5,047,314, Chari et al U.S. Patent 5,087,554, Bagchi et al U.S. Patent 5,091,296, Mihayashi et al U.S. Patent 5,100,771, Bagchi et al U.S. Patent 5,104,776, Tanji et al U.S. Patent 5,110,718, Mihayashi U.S. Patent 5,112,729, Furusawa et al U.S. Patent 5,120,637, Wolff U.S. Patent 5,134,061, Schofield et al U.S. Patent 5,188,926, Endo et al U.S. Patent 5,192,130, Merkel et al U.S. Patent 5,192,646, Hasebe U.S. Patent 5,223,385, Texter et al U.S. Patent 5,234,807, Merkel et al U.S. Patent 5,250,405, Takahashi et al EPO 0 232 770, Fehnel et al EPO 0 266 410, Takahashi et al EPO 0 276 319, Tachibana et al EPO 0 285 991, Fukuzawa EPO 0 332 165, Takahashi EPO 0 353 714, Mittel et al EPO 0 379 893, Nishijima EPO 0 382 443, Yamazaki et

al. EPO 0 465 003, Tomiyama EPO 0 471 347, Beltramini et al EPO 0 483 612, Kimura et al EPO 0 502 531, Merkel et al EPO 0 523 640, Yamouchi et al EPO 0 528 435, Chiba et al EPO 0 536 663, Young et al EPO 0 548 062, Zengerle et al EPO 0 550 359, Karino et al EPO 0 554 834, Oppenheimer EPO 0 555 923, Yoshioka EPO 0 569 979, Roth et al East German DD 288 250, Zenker et al East German DD 291 168, Langen et al German DE 37 00 570, Renner German DE 37 30 557, Langen German DE 39 36 300, Young WO 92/01971, Sawyer et al WO 93/03420 and Coopes et al WO 93/04397.

## XI. Layers and layer arrangements

(1) The photographic elements can have photographic silver halide emulsion layers and other layers such as intermediate layers, barrier layers, scavenger layers, filter layers, antihalation layers, overcoat layers and subbing layers, in any order known to be useful in the photographic art.

(2) Gorokhovskii, *Spectral Studies of the Photographic Process*, Table 27a, p. 221, Focal Press, New York, discloses six possible subtractive primary dye image hue-spectral sensitivity combinations, but color photographic elements typically contain separate blue, green and red recording emulsion layers or layer units that form yellow, magenta and cyan dye images, respectively. For example, a color photographic silver halide element can typically comprise, in order, on a support, a red-sensitive silver halide emulsion layer or unit, a green-sensitive silver halide emulsion layer or unit and a blue-sensitive silver halide negative photographic silver halide film can comprise, in order, on a film support, a slow red-sensitive layer, a fast green-sensitive layer, a yellow filter layer, a slow blue-sensitive layer and a fast blue-sensitive layer, as described by Beles et al U.S. Patent 4,184,876, Ranz et al German OLS 2,704,797 and Lohman et al German OLS 2,622,923, '924 and 2,704,826. Another practiced example of a color negative photographic silver halide film can comprise, in order, on a film support, a slow red-sensitive layer, a slow green-sensitive layer, an optional yellow filter layer, a slow blue-sensitive layer, a fast red-sensitive layer, a fast green-sensitive layer, an optional yellow filter layer and a fast blue-sensitive layer. A variety of varied layer order arrangements for color photographic elements are disclosed by Kofron et al U.S. Patent 4,439,520. Yamada et al EPO 0 488 313 relates blue, green and red recording layer units in terms of their relative modulation transfer factors (MTF).

(3) Multilayer arrangements including combinations of couplers, combinations of couplers with other compounds or with other photographic parameters, and photographic elements based on other interlayer relationships are shown in Menjo et al U.S. Patent 4,500,633, Giusto et al U.S. Patent 4,582,780, Shibahara

et al U.S. Patent 4,680,253, Ogawa et al U.S. Patent 4,686,175, Saskai et al U.S. Patents 4,705,744 and 4,707,436, Deguchi et al U.S. Patent 4,746,599, Beltramini U.S. Patent 4,777,122, Matejec U.S. Patent 4,830,954, Hirose et al U.S. Patent 4,840,878, Yamagami et al U.S. Patent 4,946,767, Bowne U.S. Patent 4,960,685, Iijima et al U.S. Patent 4,977,069, Tai et al U.S. Patents 4,980,274 and 4,981,774, Hirabayashi et al U.S. Patent 5,023,169, Hasebe et al U.S. Patent 5,028,515, Hattori et al U.S. Patent 5,032,496, Ikeda et al U.S. Patent 5,034,310, Yamagami et al U.S. Patent 5,085,979, Ogawa et al U.S. Patent 5,124,241, Sasaki U.S. Patent 5,169,746, Chari U.S. Patent 5,190,851, Sakanoue et al U.S. Patent 5,212,052, Tashiro et al U.S. Patent 5,212,054, Saskai et al EPO 0 107 112, Onodera et al EPO 0 234 742, Hasebe et al EPO 0 256 537, EPO 0 270 078, Hiroshi EPO 0 270 331, EPO 0 313 083, Tadashi EPO 0 371 325, Naito EPO 0 373 382, Haraga EPO 0 437 859, Deguchi et al EPO 0 442 323, Tanaka et al EPO 0 446 060, Tosaka et al EPO 0 459 334, Ikeda et al EPO 0 474 136, Iwagaki et al EPO 0 474,166, Tobeta EPO 0 481 422, Sakurazawa et al EPO 486,965, Sakakibara et al EPO 0 459 458, Sawyer et al EPO 0 492 443, Uezawa et al EPO 0 501 464, Miyayashi et al EPO 0 502 424, Yoshioka et al EPO 0 503 587, Nakagawa et al EPO 0 510 535, Ohya et al EPO 0 530 668, Hirabayashi et al EPO 0 536 889, Naruse EPO 0 544 319, Miyayashi et al EPO 0 565 096, Naruse et al EPO 0 544 322, Naruse et al EPO 0 545 301, Miyayashi et al EPO 0 565 096, Yamada et al EPO 0 569 126, Yamada et al UK Patent Application 2,138,962 and Matejec et al German OLS 4,006,791.

## XII.

### Features applicable only to color negative

(1) The photographic elements can incorporate colored dye-forming couplers such as those employed to form integral masks for negative color images as illustrated by Hanson U.S. Patent 2,449,966, Glass et al U.S. Patent 2,521,908, Gledhill et al U.S. Patent 3,034,892, Loria U.S. Patent 3,476,563, Lestina et al U.S. Patent 3,519,429, Friedman U.S. Patent 2,543,691, Puschel et al U.S. Patent 3,028,238, Menzel et al U.S. Patent 3,061,432 and Greenhalgh U.K. Patent 1,035,959, and/or competing couplers as illustrated by Murin et al U.S. Patent 3,876,428, Sakamoto et al U.S. Patent 3,580,722, Puschel U.S. Patent 2,998,314, Whitmore U.S. Patent 2,808,329, Salminen U.S. Patent 2,742,832, Wellner et al U.S. Patent 2,689,793 and Lau U.S. Patent 4,777,120.

(2) If desired, the masks may be shifted so as to be relatively uncolored prior to processing. Recent developments in shifted and conventional masks are shown in Kaufman et al U.S. Patent 4,749,641, Lau U.S. Patent 4,777,120, Ichijima et al U.S. Patent 5,049,474, Okawa et al U.S. Patent 5,112,730, Kida U.S. Patent 5,219,719, Hirabayashi et al U.S. Patent 5,238,797, Kiyotoshi et al EPO 0 232 101, Kobayashi et al EPO 0 423 727, Miyayashi et al EPO 0 451 859, Ishii et al EPO 0 456 181, Hirabayashi et al EPO 0 529 811, Kida et al EPO 0 530 011,

Hirabayashi et al. EPO 0 430 039; Yamazaki et al. EPO 0 539 023 and Mooberry et al. WO 92/11535.

(3) Combinations of emulsions or grain morphology and couplers are shown in Fujita et al. U.S. Patent 4,640,890, Yagi U.S. 5,183,730, Heki et al. EPO 0 421 426, Nakatsugawa et al. EPO 0 510 898, and Inoue EPO 0 549 198.

(4) Combinations of couplers with other compounds in the same or adjacent layers are shown in Sasaki et al. U.S. Patent 4,774,166; Merkel U.S. Patent 4,808,502; Wagner et al. U.S. Patent 4,810,625; Isakouge et al. U.S. Patent 4,865,959; Nishijima U.S. Patent 4,868,100; Aoki et al. U.S. Patent 4,898,812; Merkel U.S. Patent 4,945,321; Hamm U.S. Patent 4,946,765; Merkel et al. U.S. Patent 4,973,535; Ohki U.S. Patent 4,978,606; Tanji et al. U.S. Patent 5,077,188; Langen et al. EPO 0 442 029; Mihaydshi EPO 0 456 257; Mihaydshi et al. EPO 0 530 681; Sato et al. EPO 0 554 027; Mader et al. DE 3,626,221, and Hubner et al. DE 3,913,404.

(5) Direct positive color images may be formed with couplers described in Heki et al. U.S. Patent 4,863,839; Deguchi U.S. Patent 5,153,107; Suzuki et al. EPO 0 264 192; Heki et al. EPO 0 267 482, and Hirano et al. EPO 0 450 637.

(6) Specialized color systems are shown in Sato et al. U.S. Patent 4,880,730, and Yoshizawa et al. U.S. Patent 4,994,345, and a chronogenic system for producing a black and white image is shown in Edwards et al. WO 93/12465.

### XIII. Features applicable only to color positive

#### A. Direct-positive imaging

(1) A direct-positive image is understood in photography to be a positive image that is formed without first forming a negative image. T.H. James, editor, *The Theory of the Photographic Process*, 4th Edition, Macmillan, New York, 1977, Chapter 7, reviews imaging mechanisms that can be employed for direct-positive imaging, with the two types of mechanisms most commonly employed appearing under the headings: 3. Prefogged Direct-Positive Photobleach Materials (hereafter referred to as prefogged direct-positive) and 7. Internal Image Desensitization (hereafter referred to as internal image direct-positive).

(2) Prefogged direct-positive emulsions rely on the hole produced by photon capture to bleach silver (fog) from the surface of the grains, thereby rendering them nondevelopable. To prevent the electron released by photon capture from contributing to surface latent image formation it is common practice to adsorb an electron trapping dye on the grain surface. Electron trapping dyes are sometimes referred to as desensitizing dyes, since they are used to desensitize negative-working emulsions. Development of prefogged direct-positive emulsions can be undertaken by the conventional techniques employed to develop negative-working emulsions.

(3) Internal image direct-positive emulsions rely on the internal latent image formed by exposure to retard or arrest development in an environment in which unexposed grains are developed (e.g., in the presence of light or a nucleating agent). Internal image direct-positive emulsions typically employ the same spectral sensitizing dyes as negative-working emulsions. Typically development is undertaken by the conventional techniques employed for the surface development of negative-working emulsions, but with a nucleating agent adsorbed to the grain surfaces. Research Disclosure, Vol. 151, Nov. 1976, Item 15162, provides an illustration of internal image-direct positive imaging, also sometimes referred to as direct reversal imaging, in the context of (but not limited to) color image transfer imaging.

(3) The following are illustrative of recent publications relating to direct-positive imaging: Sensitizing dyes particularly for direct-positive elements using fogged emulsions are described in Kojima et al. U.S. Patent 4,756,995 (direct reversal element with arylidene filter dyes), Deguchi et al. EPO 0 322 702 (with N-arylalkyl or aryl substituted pyrazolone oxonol filter dyes), Jimbo et al. EPO 0 360 289 (with azarolone dyes of specific absorption wavelength requirements), Nakamura et al. EPO 0 536 647. Sensitizing dyes particularly for internal image direct-positive emulsions are described in Yoshida et al. U.S. Patent 4,857,445 (internal latent image forming emulsion sensitized with benzoxazole carbocyanine dyes), Inoue et al. U.S. Patent 4,925,777 (element with internal latent image emulsion and specific cyanine or hemicyanine compounds to provide high maximum color density and low minimum color density), Yoshizawa et al. U.S. Patent 4,925,780 (internal latent image forming emulsion with particular sensitizers plus absorber dyes). Sensitizing dyes for fogged direct positive emulsions are described in Wheeler U.S. Patent 4,355,098 (fogged emulsion with supersensitizing dye combinations), Inoue et al. U.S. Patent 4,539,291 (fogged emulsion with sensitizer combinations including phenazine compounds), Wheeler U.S. Patent 4,701,398 (fogged emulsions with indolizine sensitizers), Weaver U.S. Patent 4,839,271 (fogged emulsion sensitized with indolocyanine dyes), Dewanckele et al. U.S. Patent 5,198,333 (fogged emulsion with ultraviolet light sensitizers).

(4) Particular methods for processing internal image direct-positive emulsions, are described, for example, in Heki et al. U.S. Patent 4,863,839 (processing with non-diffusible coupler while applying fogging treatment), Inoue et al. U.S. Patent 4,871,653 (processing in presence of nucleating agent and a mercapto group containing compound), Heki et al. U.S. Patent 4,880,729 (processing in presence of nucleating agents containing quaternary heterocyclic compound plus hydrazine compound), Inoue et al. U.S. Patents 4,952,483 (method for processing direct positives images using nucleator and nucleator accelerator) and

4,954,427 (processing with nucleating agent and nucleating accelerator containing thioether, amino, ammonium, ether or heterocyclic groups, Ogi et al U.S. Patent 4,990,438 (direct positive element with active halide or active vinyl gelatin hardeners plus other compounds), Inoue et al U.S. Patents 4,994,364 (fogging in the presence of particular substituted hydrazines) and 4,966,836 (element with bicyclic nucleator and heterocyclic nucleating accelerator), Hayashi et al U.S. Patent 5,015,561 (processing direct positive elements containing particular nucleating agents and sensitizing dyes, in presence of nucleation accelerator), Hayashi deceased et al U.S. Patent 5,035,984 (method for processing direct positives using nucleators), Shuto et al U.S. Patent 5,110,719 (with sulfone compound for reducing minimum density without reducing maximum density), Kuwashima et al U.S. Patent 5,213,952 (processing element with sensitizing dye and a salt thereof which has particular extinction coefficient), Kamitakahara et al EPO 0 262 930 (particular processing conditions for elements having silver chloride shells of core-shell emulsions and having a heterocyclic mercapto compound).

#### B. Color reversal

(1) Color reversal elements are those containing negative-working emulsions and intended to be developed first in a black-and-white developer, which does not form any image dyes, followed by a fogging step, and finally processed in a developer which can form image dyes. Components and techniques which are described as being particularly applicable to color reversal elements are described in Sowinski et al U.S. Patent 4,656,122 (fine grains blended with tabular grains), Kuwashima et al U.S. Patent 4,792,518 (color reversal paper with specified tone scale), Deguchi et al U.S. Patents 4,886,738 (with compounds to enhance push processing) and Deguchi U.S. Patent 5,024,925 (of specified red sensitivity requirements plus interimage means), Kimura et al U.S. Patent 5,128,237 (element with oxidized developer scavenger), Kim et al U.S. Patent 5,272,048 (low dispersity tabular grains), Bowne EPO 0 529 737 (element with 2-equivalent magenta dye forming coupler and blue or green filter dye), Mitsui et al EPO 0 543 403 (element containing emulsion of particular halide type plus cyclic azo to reduce mottle) Kumashiro et al 0 559 395 (color reversal material with development inhibitor released upon redox reaction) Munshi et al U.S. Patents 5,382,499 (underwater color reversal element) and 5,298,369 (element with colloidal elemental silver).

#### C. Color positives derived from color negatives

(1) Most typically a color negative film is exposed in a camera to produce a color negative image. The color negative image is then used to expose a negative-working color element that produces a viewable color positive image, typically a reflection print (e.g., color paper).

(2) Components and techniques which are described as being applicable to various types of color papers (i.e. any photographic element having a paper based or reflective support), are described in Kubota et al U.S. Patent 4,419,433 (resin coated paper including incorporated developer aminomethanesulfonic plus acid to reduce paper discoloration), Waki et al U.S. Patents 4,892,803 (processing color paper with monodispersed chloride core/shell emulsion in developer with substantially no benzyl alcohol) and 4,920,042 (low benzyl alcohol developing process for color paper containing specified sensitizing dyes), Sato et al U.S. Patent 5,252,424 (reflective support), Lacz U.S. Patent 5,254,450 (oxygen barrier for improved stability), Bagchi et al U.S. Patent 5,279,931 (fine particle coupler dispersions), Lok U.S. Patent 5,292,635 (thiosulfonate-sulfinate stabilizers to reduce fog upon aging) Schuman U.S. Patent 5,246,823 (improved antihalation layer), Szajewski U.S. Patent 5,399,469 (absorber dye); Bohan et al U.S. Patent 5,434,038 (tabular silver chloride); Edwards et al U.S. Patent 5,418,118, and Asami et al. U.S. Patent 5,422,232 (support pH of 5 to 9).

(3) Components and techniques which are described as being applicable to any photographic element which is used to form a positive image, are described in Hahn U.S. Patent 4,902,609 (color positive with negative-working emulsions and a layer sensitized to two colors) and Mitsui et al U.S. Patent 5,079,132 (exposing direct positive or reversal material from an original through a filter of specified absorption characteristics).

#### XIV.

##### Scan facilitating features

(1) The photographic elements can produce images that can be viewed by scanning. Illustrative element constructions and systems of scan signal manipulation, including techniques for maximizing the quality of image records, are disclosed by Bayer U.S. Patent 4,553,165, Urabe et al U.S. Patent 4,591,923, Sasaki et al U.S. Patent 4,631,578, Alkofer U.S. Patent 4,654,722, Yamada et al U.S. Patent 4,670,793, Klees U.S. Patent 4,694,342, Powell U.S. Patent 4,805,031, Mayne et al U.S. Patent 4,829,370, Abdulwahab U.S. Patent 4,839,721, Matsunawa et al U.S. Patents 4,841,361 and 4,937,662, Mizukoshi et al U.S. Patent 4,891,713, Petilli U.S. Patent 4,912,569, Sullivan et al U.S. Patent 4,920,501, Kimoto et al U.S. Patent 4,929,979, Klees U.S. Patent 4,962,542, Hirotsawa et al U.S. Patent 4,972,256, Kaplan U.S. Patent 4,977,521, Sakai U.S. Patent 4,979,027, Ngi U.S. Patent 5,003,494, Katsuyama et al U.S. Patent 5,008,950, Kimura et al U.S. Patent 5,065,255, Osamu et al U.S. Patent 5,051,842, Lee et al U.S. Patent 5,012,333, Sullivan et al U.S. Patent 5,070,413, Bowers et al U.S. Patent 5,107,346, Teille U.S. Patent 5,105,266, MacDonald et al U.S. Patent 5,105,469, Kwon et al U.S. Patent 5,081,692, Sutton et al U.S. Patent 5,300,413, Sutton U.S.

Patents 5,314,794 and 5,389,506, and Simons U.S. Patents 5,350,664 and 5,148,119.

(2) The photographic elements can include magnetic recording layers, such as those described in Research Disclosure, Vol. 343, Nov. 1992, item 34390. Recent additional publications relating to a transparent magnetic recording layer on a photographic element are illustrated by Sakakibara U.S. Patents 5,215,874 and 5,147,768, Kitagawa U.S. Patent 5,187,518, Nishiura U.S. Patent 5,188,789, Mori U.S. Patent 5,227,283, Yokota U.S. Patent 5,229,259, Hirose et al U.S. Patent 5,238,794, Nair et al U.S. Patent 5,457,012, Yasuo et al EPO 0 476 535, Masahiko EPO 92/123,040, Yagi et al Japanese Kokai 92/125,548, 92/146,429 and 92/163,541, and Nagayasu et al Japanese Kokai 92/125,547.

(3) The photographic elements can contain an edge region particularly adapted for scanning, such as those employed to form sound tracks, as illustrated by Sakakibara U.S. Patents 5,147,768 and 5,215,874, Kitagawa U.S. Patent 5,187,518, Nishiura U.S. Patent 5,188,789, Mori U.S. Patent 5,227,283, Yokota U.S. Patent 5,229,259 and Japanese Patent Application 92/203,098, Hirose et al U.S. Patent 5,238,794, Yasuo et al EPO 0 476 535, Masahiko EPO 0 583,787, Yagi et al Japanese Patent Application 90/291,135 and Nagayasu et al Japanese Patent Application Japanese Patent Application 90/246,923.

## XV.

### Supports

(1) The layers of the photographic elements can be coated on a variety of supports. Typical photographic supports include polymeric film, wood fiber--e.g., paper, metallic sheet and foil, glass and ceramic supporting elements provided with one or more subbing layers.

(2) Subbing layers are provided on photographic film base primarily to improve the adhesion of hydrophilic layers thereto. However, suitable subbing layers are also employed to permit stripping and application to a permanent support. Subbing layers can also serve other purposes including barrier, anti-blocking and antihalation, in addition to improving dimensional stability and antistatic properties as illustrated by the following relatively recent publications: Hattori et al U.S. Patent 5,232,825, Toya et al U.S. Patent 5,019,494, Strobel et al U.S. Patent 5,244,780, Van Thillo et al U.S. Patent 4,990,434 and EPO 0 529 697, Kanetake et al U.S. Patent 4,977,071, Suematsu et al U.S. Patent 4,965,180, Van Ooij et al U.S. Patent 5,204,219, Vermeulen et al U.S. Patent 5,194,347, Hatakeyama et al U.S. Patent 4,994,353, Ishigaki et al U.S. Patent 4,954,430, Sakata et al U.S. Patent 5,061,611, Nittel et al U.S. Patent 5,292,628, Tachibana et al 5,306,606, Melpolder et al U.S. Patent 5,308,687, Markin et al U.S. Patent 5,310,640, Stimson et al U.S. Patent 5,326,688, Takada U.S. Patent 5,352,569, Havens et al U.S. Patent 5,356,468, Takada et al U.S. Patent 5,360,708, Kurachi et al U.S.

Patent 5,364,751, Christian et al U.S. Patent 5,368,995, Kurachi et al 5,372,923, Westfal et al U.S. Patent 5,374,510, Kurachi et al 5,376,517, Jennings et al 5,376,518, Nakanishi et al U.S. Patent 5,378,592, Kudo et al U.S. Patent 5,382,494, Suzuki U.S. Patent 5,436,123, Boston et al U.S. Patent 5,439,785, Krafft et al U.S. Patent 5,443,944, Krefci et al U.S. Patent 5,496,647, Sack et al German DE 4,302,678 Yajima et al EPO 0 466 124, Valsecchi et al EPO 0 589 329, Berner et al EPO 0 616 252, Bayless et al EPO 0 631 178, Machida et al EPO 0 651 287, Taguchi EPO 0 660 174, Krefci et al EPO 0 661 362, and Miyamoto EPO 0 668 534.

(3) Overcoat layers protect photographic film against scratching, abrasion, fingerprinting, fire, water spotting, blocking, as well as providing surface texture, and glare reduction, as illustrated by the following: Jones U.S. Patent 5,037,871, Smith U.S. Patent 5,034,057, Arai U.S. Patent 5,206,128, Oikawa U.S. Patent 5,185,238, Himmelmann et al U.S. Patent 5,085,981, Bagchi et al U.S. Patent 5,393,650, Fujita et al U.S. Patent 5,415,986, Bagchi et al U.S. Patent 5,426,020, Ushiroyama et al EPO 0 494 121, Kobayashi et al EPO 0 376 655, Jones WO 91/18325, Lalvani et al German OLS 4,001,784, Lalvani et al German OLS 3,936,827, and Himmelmann German OLS 3,809,935.

(4) Typical of useful polymeric film supports are films of cellulose nitrate and cellulose esters (such as cellulose triacetate and diacetate), polystyrene, polyamides, homopolymers of vinyl chloride, poly(vinyl acetal), polycarbonate, homo- and copolymers of olefins such as polyethylene and polypropylene, and polyesters of dibasic aromatic carboxylic acids with divalent alcohols such as poly(ethylene terephthalate). Cellulose acetate photographic film supports, methods of making, and applications thereof are set forth in Riech U.S. Patent 4,992,491, Suzuki et al U.S. Patent 5,188,788, Machell et al U.S. Patent 5,219,510, Nishiura et al EPO 0 479 260 and Tsujimoto et al EPO 0 535 652. Polystyrene and liquid crystal polyester supports are illustrated by the following recent publications: Funaki et al U.S. Patent 5,188,930 and Zeroni et al U.S. Patent 5,108,666.

(5) Reflective (typically paper) supports can be employed. Typical paper supports are partially acetylated or coated with baryta and/or a polyolefin, particularly a polymer of an a-olefin containing 2 to 10 carbon atoms, such as polyethylene, polypropylene, copolymers of ethylene and propylene and the like. Polyolefins such as polyethylene, polypropylene and polyallomers--e.g., copolymers of ethylene with propylene, as illustrated by Hagemeyer et al U.S. Patent 3,478,128, are preferably employed as resin coatings over paper as illustrated by Crawford et al U.S. Patent 3,411,908 and Joseph et al U.S. Patent 3,630,740. Over polystyrene and polyester film supports as illustrated by Crawford et al U.S. Patent 3,630,742, or can be employed as unitary flexible reflection supports as illustrated

by Venor et al U.S. Patent 3,973,963. More recent publications relating to resin coated photographic paper are illustrated by Kamiya et al U.S. Patent 5,178,936, Ashida U.S. Patent 5,100,770, Harada et al U.S. Patent 5,084,344, Noda et al U.S. Patent 5,075,206, Bowman et al U.S. Patent 5,075,164, Dethlefs et al U.S. Patents 4,898,773, 5,004,644 and 5,049,595, EPO 0 507 068 and EPO 0 290 852, Saverin et al U.S. Patent 5,045,394 and German OLS 4,101,475, Uno et al U.S. Patent 4,994,357, Shigetani et al U.S. Patents 4,895,688 and 4,968,554, Tamagawa U.S. Patent 4,927,495, Wysek et al U.S. Patent 4,895,757, Kojima et al U.S. Patent 5,104,722, Katsura et al U.S. Patent 5,082,724, Nittel et al U.S. Patent 4,906,560, Thomas et al U.S. Patent 5,290,671, Dunk U.S. Patent 5,290,672, Nishikawa et al U.S. Patent 5,312,682, Kato et al U.S. Patent 5,360,707, Serizawa et al U.S. Patent 5,362,614, Miyoshi et al U.S. Patent 5,366,854, Akao U.S. Patent 5,401,562, Asami et al U.S. Patent 5,422,232, Onshima U.S. Patent 5,429,916, Nagata et al U.S. Patent 5,434,039, Dethlefs U.S. Patent 5,457,016, Miyoshi et al EPO 0 507 489, Inahata et al EPO 0 413 332, Kadowaki et al EPO 0 546 713 and EPO 0 546 711, Nishikawa et al EPO 0 648 603, Skochdopole WO 93/04400, Edwards et al WO 92/17538, Reed et al WO 92/00418 and Tsubaki et al German OLS 4,220,737.

(6) Kiyohara et al U.S. Patent 5,061,612, Shiba et al EPO 0 337,490 and EPO 0 389 266, and Noda et al German OLS 4,120,402 disclose pigments primarily for use in reflective supports. Reflective supports can include optical brighteners and fluorescent materials, as illustrated by Martic et al U.S. Patent 5,198,330, Kubota et al U.S. Patent 5,106,989, Carroll et al U.S. Patent 5,061,610 and Kadowaki et al EPO 0 484 871. Lenticular reflective supports are illustrated by Kistner U.S. Patent 5,013,621 and Shiba et al U.S. Patent 5,075,204. Embossed photographic paper is illustrated by Uehara U.S. Patent 5,212,005 and Tanaka et al U.S. Patent 5,242,786. Other recent publications relating to photographic paper include Sato et al U.S. Patent 5,234,804, Noda et al U.S. Patent 5,264,033, Dethlefs U.S. Patent 5,332,623, Otani U.S. Patent 5,409,806, Hayashi U.S. Patent 5,432,043, Dewitt EPO 0 541 457, Ogata et al EPO 0 565 002, Schoeller German OLS 4,139,251 and 3,942,733, Rohringer et al EPO 0 624 687, Tosaka et al EPO 0 653 673, and Tanaka et al EPO 0 653 674.

(7) Preferred cellulose ester supports are cellulose triacetate supports, as illustrated by Fordyce et al U.S. Patents 2,492,977, '978 and 2,739,069, as well as mixed cellulose ester supports, such as cellulose acetate propionate and cellulose acetate butyrate as illustrated by Fordyce et al U.S. Patent 2,739,070. Cellulose ester films can be formed by varied techniques, as illustrated by Malm et al U.S. Patent 3,592,671, Dotson et al U.S. Patent 3,608,059, Tuoev et al U.S. Patent 3,640,742, Dotson et al U.S. Patent 3,705,148, Schrader U.S. Patent 3,718,728 and Dresie et al U.S. Patent 3,793,043, and can

be modified for use as photographic film supports as illustrated by Grady et al U.S. Patent 3,376,149, Jacoby et al U.S. Patent 3,627,583 and Novak et al U.S. Patent 4,092,173. Incorporation of stripping aids in cellulose ester supports is described in Krall U.S. Patent 4,348,238.

(8) Preferred polyester film supports are comprised of linear polyester, such as illustrated by Alles et al U.S. Patent 2,627,088, Wellman U.S. Patent 2,720,503, Alles U.S. Patent 2,779,684 and Kibler et al U.S. Patent 2,901,466. Polyester films can be formed by varied techniques as illustrated by Alles, cited above, Cierkas et al U.S. Patent 3,663,683 and Williams et al U.S. Patent 3,504,075, and can be modified for use as photographic film supports by subbing, etc., as illustrated by Vanstappen U.S. Patent 3,227,576, Nadeau et al U.S. Patents 3,143,421 and 3,501,301, Reedy et al U.S. Patent 3,589,905, Babbitt et al U.S. Patent 3,850,640, Bailey et al U.S. Patent 3,888,678, Hunter U.S. Patent 3,904,420, Mallinson et al U.S. Patent 3,928,697, Van Paesschen et al U.S. Patent 4,132,552, Schrader et al U.S. Patent 4,141,735, McGrail et al U.S. Patent 4,304,851, Kreil et al U.S. Patent 4,594,262, and Bayless et al U.S. Patent 4,645,731. The polyester film support can be discharge-treated and subbed with a polymer-gelatin composition cross-linkable with a gelatin hardener, as illustrated by Ponticello et al, U.S. Patents 4,689,359 and 4,695,532. Polyester supports and related features are further illustrated by the following recent publications: Maier et al U.S. Patent 5,034,263 and 4,994,312, Fukazawa U.S. Patent 5,225,319, Kawamoto et al U.S. Patent 4,978,740, Van Cappellen et al U.S. Patent 4,892,689, Hirooka et al U.S. Patent 5,215,825, Nitta et al U.S. Patent 5,188,774, Verheijen et al U.S. Patent 5,185,426, Stevens et al U.S. Patent 4,994,214, Satako et al U.S. Patent 4,910,235, Brozek et al U.S. Patent 5,138,024, Kiyohara et al U.S. Patents 4,898,897 and 4,847,149 and EPO 0 327 768, Greener et al U.S. Patent 5,288,601, Kawamoto U.S. Patent 5,294,473, Sumner, Jr. et al U.S. Patent 5,296,587, Jones et al U.S. Patent 5,310,857, Kawamoto U.S. Patents 5,350,829 and 5,368,997, Kobayashi et al U.S. Patent 5,372,925, Tsou et al U.S. Patent 5,385,704, Yajima et al U.S. Patent 5,387,501, Marien et al U.S. Patent 5,411,843, Grace et al U.S. Patent 5,425,980, Satake et al EPO 0 334 367, Nishiura et al EPO 0 496 346, Sakamoto et al EPO 0 510 654, Mochizuki et al EPO 0 517 506, Ueda et al EPO 0 518 260, Kobayashi et al EPO 0 545 439, EPO 0 566 094 and 0 572 275, Yajima et al EPO 0 568 268, Ueda et al EPO 0 562 533, Mostaert et al EPO 0 559 244, Araki et al EPO 0 568 268, Stevens et al EPO 0 582 750, Murayama EPO 0 583 787, Verheijen EPO 0 606 663, Nakanishi et al EPO 0 618 488, Kimura et al EPO 0 619 516, Okamoto et al EPO 0 636 928, Kawamoto et al EPO 0 658 804, Kawamoto et al EPO 0 674 218, Hashimoto et al EPO 0 677 778, Yajima et al EPO 0 681 211, Bennett et al WO 94/13480, and in Tetsuro et al German OLS 3,800,130.



(9) The photographic elements can employ supports which are resistant to dimensional change at elevated temperatures. Such supports can be comprised of linear condensation polymers which have glass transition temperatures above about 190°C, preferably 220°C, such as polycarbonates, polycarboxylic esters, polyamides, polysulfonamides, polyethers, polyimides, polysulfonates and copolymer variants, as illustrated by Hamb U.S. Patents 3,634,089 and 3,772,405; Hamb et al U.S. Patents 3,725,070 and 3,793,249; Wilson Research Disclosure, Vol. 118, February, 1974; Item 11833, and Vol. 120, April, 1974, Item 12046; Conklin et al Research Disclosure, Vol. 120, April, 1974, Item 12012; Product Licensing Index, Vol. 92, December, 1971, Items 9205 and 9207; Research Disclosure, Vol. 101, September, 1972, Items 10119 and 10148; Research Disclosure, Vol. 106, February, 1973, Item 10613; Research Disclosure, Vol. 107, January, 1974, Item 11709, and Research Disclosure, Vol. 134, June, 1975, Item 13455.

## XVI.

### Exposure

(1) The photographic elements can be imagewise-exposed with various forms of energy which encompass the ultraviolet and visible (e.g., actinic) and infrared regions of the electromagnetic spectrum, as well as electron-beam and  $\beta$  radiation,  $\gamma$ -ray, x-ray,  $\alpha$  particle, neutron radiation and other forms of corpuscular and wave-like radiant energy in either noncoherent (random phase) forms or coherent (in phase) forms as produced by lasers. Exposures can be monochromatic, orthochromatic or panchromatic. Imagewise exposures at ambient, elevated or reduced temperatures and/or pressures, including high- or low-intensity exposures, continuous or intermittent exposures, exposure times ranging from minutes to relatively short durations in the millisecond to microsecond range and solarizing exposures, can be employed within the useful response ranges determined by conventional sensitometric techniques, as illustrated by T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 4, 6, 17, 18 and 23.

(2) The photographic elements can capture images in exposure structures intended for repeated use or exposure structures intended for limited use, variously referred to as single use cameras, lens with film or photosensitive material package units. Limited use exposure structures are illustrated by Fujimura et al U.S. Patent 4,766,451, Vandemoere (et al) U.S. Patents 4,801,957 and 4,901,097, Ushiro et al U.S. Patent 4,812,866, Sasaki et al U.S. Patent 4,827,298, Shiba (et al) U.S. Patents 4,827,298, 4,849,325, 4,886,469, 5,037,728 and 5,148,198 and EPO 0 460 600, Ohmura et al U.S. Patents 4,833,495 and 4,855,774, Mochida et al U.S. Patent 4,884,087, Takei et al U.S. Patent 4,890,130, Ikenoue U.S. Patent 5,187,514, Iwagaki (et al) U.S. Patent 5,223,871 and EPO 0 556 812, Yagi et al U.S. Patent

5,258,269 and EPO 0 553 785, Iijama et al EPO 0 537 908, Nozawa EPO 0 578 225 and Esaki et al EPO 0 579 228, as well as the following Japanese Patent Applications: 88/118,157, 88/194,254, 88/194,255, 88/194,256, 89/024,250, 89/072,153, 89/096,847, 89/116,638, 89/224,750, 89/291,248, 90/032,331, 90/043,536, 90/059,741, 90/201,341, 90/220,041, 90/250,051, 90/272,449, 91/083,053, 91/107,143, 91/153,241, 91/153,242, 91/153,243, 91/230,157, 91/233,446, 91/233,447, 91/240,041, 91/240,042, 91/240,043, 91/240,044, 93/002,242, 93/011,412, 93/045,812, 93/134,355, 93/134,365, 93/165,151, 93/188,448, 93/210,201, 93/210,203, 93/232,643, 93/232,644, 93/265,154, 93/307,235, 94/082,980 and 94/082,981.

## XVII. Physical development systems

### A. Non-specific processing features

(1) The photographic elements can contain or be processed to contain, as by direct development, an imagewise distribution of a physical development catalyst. The catalyst-containing element can be processed by pre- or postfixation physical development in the presence of an image-forming material such as a salt or complex of a heavy metal ion (e.g., silver, copper, palladium, tellurium, cobalt, iron and nickel) which reacts with a reducing agent such as a silver halide developing agent at the catalyst surface. Either the absorption or solubility of the image-forming material can be altered by physical development. The image-forming material and/or reducing agent can be incorporated in the photographic element, in a separate element associated during processing or, most commonly, in an aqueous processing solution. The processing solution can contain addenda to adjust and buffer pH, ionic surfactants and stabilizers, thickening agents, preservatives, silver halide solvents and other conventional developer addenda.

(2) Such physical development systems are illustrated by Archambault et al U.S. Patent 3,576,631, Silverman U.S. Patent 3,591,609, Yudelison et al U.S. Patents 3,650,748, 3,719,490 and 3,598,587, Case U.S. Patent 3,512,972, Charles et al U.S. Patent 3,253,923, Wyman U.S. Patent 3,893,857, Lelental Research Disclosure, Vol. 156, April, 1977, Item 15631 and U.S. Patent 3,935,013 and Weide et al U.K. Patent 1,125,646, each particularly illustrating heavy metal salts and complexes, Cole U.S. Patent 3,390,998 and Jonker et al U.S. Patent 3,223,525, particularly illustrating processing solutions containing ionic surfactants and stabilizers, and Bloom U.S. Patent 3,578,449, particularly illustrating processing solutions containing silver halide solvents. Physical developers producing dye images can be employed as illustrated by Gysling et al U.S. Patents 4,042,392 and 4,046,569. Physical development can be used to provide images with an antique look using image receiving materials containing a nacreous pigment according to Vermeulen et al U.S. Patent 5,340,692.

## XVIII. Chemical development systems

### A. Non-specific processing features

(1) The light-sensitive silver halide contained in the photographic elements can be processed following exposure to form a visible image by associating the silver halide with an aqueous alkaline medium in the presence of a developing agent contained in the medium or the element. Processing formulations and techniques are described in L. P. Mason, *Photographic Processing Chemistry*, Focal Press, London, 1966; *Processing Chemicals and Formulas*, Publication J-1, Eastman Kodak Company, 1973; *Photo-Lab Index*, Morgan and Morgan, Inc., Dobbs Ferry, New York, 1977; and *Neblette's Handbook of Photography and Reprography Materials, Processes and Systems*, VanNostrand Reinhold Company, 7th Ed., 1977.

(2) Included among the processing methods are web processing as illustrated by Fregillus et al U.S. Patent 3,179,517, stabilization processing as illustrated by Herz et al U.S. Patent 3,220,839, Cole U.S. Patent 3,615,511, Shipton et al U.K. Patent 1,258,906 and Haist et al U.S. Patent 3,647,453, monobath processing as described in Haist, *Monobath Manual*, Morgan and Morgan, Inc., 1966, Schuler U.S. Patent 3,240,603, Haist et al U.S. Patents 3,615,513 and 3,628,955 and Price U.S. Patent 3,723,126, infectious development as illustrated by Milton U.S. Patents 3,294,537, 3,600,174, 3,615,519 and 3,615,524, Whiteley U.S. Patent 3,516,830, Drago U.S. Patent 3,615,488, Salesin et al U.S. Patent 3,625,689, Illingsworth U.S. Patent 3,632,340, Salesin U.K. Patent 1,273,030 and U.S. Patent 3,708,303, hardening development as illustrated by Allen et al U.S. Patent 3,232,761, roller transport processing as illustrated by Russell et al U.S. Patents 3,025,779 and 3,515,556, Masseth U.S. Patent 3,573,914, Taber et al U.S. Patent 3,647,459 and Rees et al U.K. Patent 1,269,268, alkaline vapor processing as illustrated by Product Licensing Index, Vol. 97, May, 1972, Item 9711, Goffe et al U.S. Patent 3,816,136 and King U.S. Patent 3,985,564, metal-ion development as illustrated by Price, *Photographic Science and Engineering*, Vol. 19, No. 5, 1975, pp. 283-287 and Vought Research Disclosure, Vol. 150, October, 1976, Item 15034, reversal processing as illustrated by Henn et al U.S. Patent 3,576,633, and surface application processing as illustrated by Kitz U.S. Patent 3,418,132. High chemical efficiency and low carry-out loss in photographic processing are provided by the multistage contacting process of Hahn U.S. Patent 4,719,173.

(3) The photographic elements can be processed to form dye images which correspond to or are reversals of the silver halide rendered selectively developable by imagewise exposure.

(4) Photographic chemicals may be utilized in solid forms such as tablets, powders and granules as described in Emoto et al U.S. Patent 3,833,377, Katz U.S. Patent 3,867,151, Emoto et al U.S. Patent 3,981,732, Hayashi et al U.S. Patent 4,022,621,

Speers U.S. Patent 4,029,510, Kapecki et al U.S. Patent 4,414,307, Libicky et al U.S. Patent 4,546,069, Tirel et al U.S. Patents 4,687,846 and 4,732,981, Long et al U.S. Patent 4,753,869, Fruge et al U.S. Patent 4,816,384, Ishikawa et al U.S. Patent 4,880,728, Tirel et al U.S. Patent 4,917,992, Kühnert et al U.S. Patent 4,923,786, Nebe et al U.S. Patent 4,925,771, Reuter et al U.S. Patent 5,135,840, Ueda U.S. Patent 5,336,588, Haraguchi et al U.S. Patent 5,409,805, Finch EPO 0 256 443, Kühnert et al EPO 0 358 034 and EPO 0 358 035, Kühnert EPO 0 407 752, Abe EPO 0 456 220, Tanaka et al EPO 0 469 877, Reuter et al EPO 0 472 007, Kuse et al EPO 0 509 807, EPO 0 538 793, Yoshimoto EPO 0 540 296, Tsuchiya EPO 0 542 283, Yoshimoto et al EPO 0 545 645, Tsuchiya EPO 0 547 796, Yoshida EPO 0 546 778, Tsuchiya et al EPO 0 611 986, Ishida et al EPO 0 611 987, Yamashita EPO 0 611 989, Tsuchiya EPO 0 624 821, Yamashita et al EPO 0 640 872, Ishida et al EPO 0 654 708, Haraguchi et al EPO 0 657 778, Deguchi et al EPO 0 667 559, Ueda et al EPO 0 668 536, Yoshimoto EPO 0 674 219, Ueda et al EPO 0 678 781, Deguchi EPO 0 678 782, Takamura EPO 0 679 940, Ishida EPO 0 681 217, Deguchi EPO 0 682 289, Tsuchiya et al EPO 0 687 950, Deguchi et al EPO 0 687 951, Tsuchiya et al EPO 0 691 571, German OLS 2,541,519, Hengefeld German OLS 3,515,440, Kühnert German OLS 3,920,920, and Japanese Patent Applications JP 49/131137, JP 54/012329, JP 60/153040, JP 63/177133, and JP 4/085534.

(5) The photographic elements can contain development modifiers in the silver halide emulsion and other developer-permeable layers either to accelerate or restrain development. Such modifiers can also be contained in the developing solution.

(6) Development accelerators of the poly(alkylene oxide) type are disclosed by Blake et al U.S. Patents 2,400,532 and 2,423,549, Blake U.S. Patent 2,441,389, Chechak et al U.S. Patent 2,848,330, Howe U.K. Patent 805,827, Piper U.S. Patents 2,886,437 and 3,017,271, Carroll et al U.S. Patents 2,944,900 and 2,944,902, Dersch et al U.K. Patent 1,030,701 and U.S. Patents 3,006,760, 3,084,044 and 3,255,013, Beavers U.S. Patent 3,039,873, Popeck et al U.S. Patent 3,044,874, Hart et al U.S. Patent 3,150,977, Willems et al U.S. Patent 3,158,484, 3,523,796 and 3,523,797, Beavers et al U.S. Patents 3,253,919 and 3,426,029, Goffe U.S. Patent 3,294,540, Milton U.S. Patent 3,615,519, Grabhoefer et al U.S. Patent 3,385,708, Mackey et al U.S. Patents 3,532,501 and 3,597,214, Willems U.S. Patent 3,552,968, Huckstadt et al U.S. Patent 3,558,314, Sato et al U.S. Patent 3,663,230, Yoneyama et al U.S. Patent 3,671,247 and Pollet et al U.S. Patent 3,947,273 and U.K. Patent 1,455,413.

(7) Representative development accelerators additionally comprise carboxylic and sulfonic acid compounds and their salts, aliphatic amines, carbamates, adducts of a thioamine with an aldehyde, polyamines, polyamides, polyesters, aminophenols, polyhydroxybenzenes, thioethers and thioamides, poly(vinyl lactams), poly(N-vinyl-2-oxazolidone), protamine sulfate, pyrazo-

lidones, pyrazolidone/cyclodextrin complexes, dihydropyridine compounds, hydroxyalkyl ether derivatives of starch, sulfite ester polymers, bis-sulfonyl alkanes, 1,4-thiazines and thioarbanate, as illustrated by U.K. Patents 1,019,693 and 1,140,741, Weyerts U.S. Patents 2,367,549 and 2,380,280, Dersch et al U.S. Patent 3,446,618, Mowrey U.S. Patent 3,904,413, Jones et al U.S. Patents 3,128,183 and 3,369,905, Arai et al U.S. Patents 3,782,946, 3,801,323, 3,804,624 and 3,822,130, Nishio et al U.S. Patent 3,163,536, Beavers et al U.S. Patents 3,330,661 and 3,305,363, Willems et al U.S. Patent 3,502,472, Huckstadt et al U.S. Patent 3,617,280, Plakunov et al U.S. Patent 3,708,302, Beavers U.S. Patent 3,046,135, Nakajima et al U.S. Patent 3,429,707, Minsk U.S. Patents 3,046,132 and 1,133 and Minsk et al U.S. Patent 3,813,247, Rogers et al U.S. Patent 3,192,044, Janssen et al U.S. Patent 3,718,464, Williams et al U.S. Patent 3,021,215, Dann et al U.S. Patents 3,038,805 and 3,046,134, Graham et al U.S. Patent 3,046,129, Thompson U.S. Patent 3,419,392, Lovett et al U.S. Patents 3,057,724 and 3,165,552, Thompson et al U.S. Patent 3,419,393, Motter U.S. Patent 3,506,443, Froehlich U.S. Patent 3,574,709, Sato et al U.S. Patent 3,625,697, Timmerman et al U.S. Patent 3,986,877, DeMunck et al U.S. Patent 3,615,516, Dersch U.S. Patent 3,006,762, Warren U.S. Patent 2,740,713, Hood et al U.S. Patent 2,751,297, Kennard et al U.S. Patents 2,937,090, 3,192,046 and 3,212,899, Munshi et al U.S. Patent 3,893,862, Holt U.K. Patent 1,352,196, Chiesa et al U.S. Patent 3,068,102, Waki et al U.S. Patent 5,118,593, Benard et al U.S. Patent 4,752,560, Nadral et al U.K. Patent Application 2,261,740, Sniadoch U.S. Patent 5,041,367 and Stewart et al U.S. Patent 3,625,699. Accelerators may also contain the grain-active attachment groups of Matejcek et al U.S. Patent 4,985,351.

(8) Representative development accelerators also comprise cationic compounds, disulfides, imidazole derivatives, inorganic salts, surfactants, thiazolidines, triazines and triazoles of the type disclosed by Carroll et al U.S. Patents 2,271,622, 2,275,727 and 2,288,226, Carroll U.S. Patents 2,271,623 and 3,062,645, Allen et al U.S. Patent 2,299,782, Beavers et al U.S. Patents 2,940,851, 2,940,855 and 2,944,898, Burness et al U.S. Patent 3,061,437, Randolph et al U.K. Patent 1,067,958, Grabhoefer et al U.S. Patent 3,129,100, Burness U.S. Patent 3,189,457, Willems et al U.S. Patent 3,532,499, Huckstadt et al U.S. Patents 3,471,296, 3,551,158, 3,598,590, 3,615,528, 3,622,329 and 3,640,715, Yoneyama et al U.S. Patent 3,772,021, Nishio et al U.S. Patent 3,615,527, Nakajima et al U.S. Patent 4,001,021, Hara et al U.S. Patent 3,808,003, Sainsbury et al U.S. Patent 2,706,157, Beavers U.S. Patent 3,901,712, Milton U.K. Patent 1,201,054, Snellman et al U.S. Patent 3,502,473, van Stappen U.S. Patent 3,923,515, Popeck et al U.S. Patent 2,915,395, Suzuki EPO 0 508 390 and Ebato et al U.S. Patent 3,901,709.

(9) Representative of development restrainers are cationic compounds of the type disclosed by Douglas et al U.K. Patent 946,476 and Becker U.S. Patent 3,502,467, esters of the type disclosed by Staud U.S. Patent 2,119,724, lactams of the type disclosed by DeMunck et al U.K. Patent 1,197,306, mercaptans and chiones as illustrated by U.K. Patent 854,693, Rogers et al U.S. Patent 3,265,498, Abbott et al U.S. Patent 3,376,310, Greenhalgh et al U.K. Patent 1,157,502, Grasshoff et al U.S. Patent 3,674,478, Salesin U.S. Patent 3,708,303, Luckey U.S. Patent 3,695,881, Stark et al U.K. Patent 1,457,664, Oniyama et al U.S. Patent 3,819,379, Bloom et al U.S. Patent 3,856,520 and Taber et al U.S. Patent 3,647,459, polypeptides as illustrated by Mueller U.S. Patent 2,699,391, poly(alkylene oxide) derivatives of the type disclosed by Blake et al U.S. Patent 2,400,532, Sprung U.S. Patent 3,471,297, Whiteley U.S. Patent 3,516,830 and Milton U.S. Patent 3,567,458, sulfoxides of the type disclosed by Herz Research Disclosure, Vol. 129, January, 1975, Item 12927, thiazoles as disclosed by Graham U.S. Patent 3,342,596, nitroindazoles as disclosed by Dewanchele et al U.S. Patent 5,236,815 and diazoles, triazoles and imidazoles as disclosed by Research Disclosure, Vol. 131, March, 1975, Item 13118.

(10) Hydroquinone compounds and derivatives may be used to modify development as described in Kajiwara et al U.S. Patent 4,963,466, Naruse et al U.S. Patent 5,024,924, Ohki et al U.S. Patent 5,104,774 and Sakai et al U.S. Patent 4,945,031.

#### B. Color-specific processing systems

(1) Multicolor reversal dye images can be formed in photographic elements having differentially spectrally sensitized silver halide layers by black-and-white development followed by (i) where the elements lack incorporated dye image formers, sequential reversal color development with developers containing dye image formers such as color couplers, as illustrated by Kodak Kodachrome K-14 process, Mannes et al U.S. Patent 2,252,718, Schwan et al U.S. Patent 2,950,970 and Pilato U.S. Patent 3,547,650, (ii) where the elements contain incorporated dye image formers such as color couplers, a single color development step as illustrated by the Kodak Ektachrome E4 and E6 and Agfa Process 44 described in British Journal of Photography Annual, 1977, pp. 194-197, Using Kodak Chemicals, Process E-6, Fifth Edition, Publication Z-119, 1993, and AGFACHROME Process 44, Handbuch Verarbeitungsrichtlinie, Manual Process Monitoring, Manuel Controle due traitement, October, 1990, Kodak color print reversal process R-3, and Kodak motion picture process VNF.; and (iii) where the photographic elements contain bleachable dyes, silver-dye-bleach processing as illustrated by the Cibachrome P-10 and P-18 processes described in the British Journal of Photography Annual, 1977, pp. 209-212. Variations on traditional reversal processing are described in Wernicke et al U.S. Patent 5,006,439 and Wernicke EPO 0 433 812.

(2) The photographic elements can be adapted for direct color reversal processing (i.e., production of reversal color images without prior black-and-white development) as illustrated by U.K. Patent 1,075,385, Barr U.S. Patent 3,243,294, Hendess et al U.S. Patent 3,647,452, Fuschel et al German Patent 1,257,570 and U.S. Patents 3,457,077 and 3,467,520, Accary-Venet et al U.K. Patent 1,132,736, Schranz et al German Patent 1,259,700, Marx et al German Patent 1,259,701, Muller-Bore German OLS 2,005,091, Ueda et al U.S. Patent 4,956,267 and Nakazyo et al U.S. Patent 5,128,238.

(3) Multicolor dye images which correspond to the silver halide rendered selectively developable by imagewise exposure, typically negative dye images, can be produced by processing as illustrated by the Kodacolor C-22, the Kodak Flexicolor C-41 and the Agfacolor processes described in *British Journal of Photography Annual*, 1977, pp. 201-205 and *British Journal of Photography Annual*, 1988, pp. 196-198, Kodak motion picture film processes ECN-2, ECN-2a and ECN-2b, and the Kodak ECP Process as described in Kodak Publication No. H-24, *Manual For Processing Eastman Color Films*. The photographic elements can also be processed by the Kodak Ektaprint 2 Process as described in Kodak Publication No. 2-122, the Kodak Ektaprint-3 and -300 processes as described in Kodak Color Dataguide, 5th Ed., 1975, pp. 18-19, and the Agfa color process as described in *British Journal of Photography Annual*, 1977, pp. 205-206, such processes being particularly suited to processing color print materials, such as resin-coated photographic papers, to form positive dye images. Rapid-access processing of color print materials employing high-chloride silver halide emulsions, such as Process RA-4, is described in the *British Journal of Photography Annual*, 1988, pp. 198-199, Vincent et al WO 87/04534 and U.S. Patent 4,892,804, Koshimizu et al U.S. Patent 4,774,167, Ishikawa et al U.S. Patents 4,851,326 and 4,876,174, Wernicke U.S. Patent 4,925,778, Fujimoto et al U.S. Patent 4,965,175, Ishikawa et al U.S. Patent 4,968,588, Wernicke et al U.S. Patent 4,997,749, Meckl et al U.S. Patent 5,021,326, Kuse et al U.S. Patent 5,028,517, Wernicke U.S. Patent 5,063,144, Yoshida et al U.S. Patent 5,077,180, Fujimoto et al U.S. Patent 5,091,292, Furusawa et al U.S. Patent 5,110,714, Yoshida et al U.S. Patent 5,153,111, Kobayashi et al EPO 0 243 100, Wernicke et al EPO 0 312 893, and Satake et al EPO 0 468 781. A method for coating development is described in Iwano U.S. Patent 5,200,302. The use of more than one developer bath is described in Hassler et al EPO 0 365,955 and Wernicke et al EPO 0 436 917.

(4) The photographic elements can be processed in the presence of reducible species such as transition metal ion complexes (e.g. cobalt(III) and ruthenium(III)) complexes containing amine and/or ammine ligands) and peroxy compounds (e.g. hydrogen peroxide and alkali metal perborates and percarbonates).

(5) Dye images can be formed or amplified by processes which employ in combination with a dye-image-generating reducing agent an inert transition metal-ion complex oxidizing agent, as illustrated by Bissonette U.S. Patents 3,748,138, 3,826,652, 3,862,842 and 3,989,526 and Travis U.S. Patent 3,765,891, and/or a peroxide oxidizing agent as illustrated by Matejec U.S. Patent 3,674,490, *Research Disclosure*, Vol. 116, December, 1973, Item 11660, and Bissonette *Research Disclosure*, Vol. 148, August, 1976, Items 14836, 14846 and 14847. Such processes are sometimes known as "amplification" or "redox amplification" processes. The photographic elements can be particularly adapted to form dye images by such processes as illustrated by Dunn et al U.S. Patent 3,822,129, Bissonette U.S. Patents 3,834,907 and 3,902,905, Bissonette et al U.S. Patent 3,847,619, Mowrey U.S. Patent 3,904,413, Hirai et al U.S. Patent 4,880,725, Iwano U.S. Patent 4,954,425, Marsden et al U.S. Patent 4,983,504, Evans et al U.S. Patent 5,246,822, Marsden et al U.S. Patent 5,260,184, Twist U.S. Patents 5,324,624 and 5,358,830, Fyson U.S. Patent 5,354,647, Marsden U.S. Patent 5,418,117, Fyson EPO 0 487 616, Bee et al EPO 0 616 255, Twist EPO 0 620 487, EPO 0 654 706 and EPO 0 654 707, Tannahill et al WO 90/13059, Marsden et al WO 90/13061, Grimsey et al WO 91/16666, Fyson WO 91/17479, Marsden et al WO 92/01972, Tannahill WO 92/05471, Henson WO 92/07299, Twist WO 93/01524 and WO 93/11460 and Wingender et al German OLS 4,211,460.

(6) The presence of transition metal-ion complexes can accelerate silver halide development as illustrated by Bissonette U.S. Patent 3,748,138, Beavers U.S. Patent 3,901,712 and Price U.S. Patent 3,964,912, can bleach silver images as illustrated by Bissonette U.S. Patent 3,923,511 and *Research Disclosure*, Item 14846, and can be employed to form tanned colloid images, as illustrated by Bissonette U.S. Patent 3,856,524 and McGuckin U.S. Patent 3,862,855.

(7) The peroxide oxidizing agents can be employed to form vesicular images as illustrated by Weyde U.S. Patent 3,615,491, Weyde et al U.K. Patent 1,329,444 and U.S. Patent 3,765,890, Meyer et al U.K. Patent 1,332,693, Liebe et al German OLS 2,420,521 and Matejec et al U.S. Patent 3,776,730.

(8) A particularly efficient method for processing silver halide materials uses a low volume thin tank processor. A low volume thin tank processor provides a small volume for holding processing solution. As a part of limiting the volume of the processing solution, a narrow processing channel is provided. The processing channel, for a processor used for photographic paper, should have a thickness equal to or less than about 50, preferably less than 10, times the thickness of paper being processed. In a processor for processing photographic film, the thickness of the processing channel should be equal to or less than about 100, preferably 18, times the thickness of photosensitive film. The total amount of processing solution in the entire processing system for a particular module is such that the total

## XIX. Development

## A. Developing Agents

The developing solution, and in some cases the photographic elements, can contain organic or inorganic developing agents or mixtures thereof. Representative developing agents are disclosed by T. H. James, *The Theory of the Photographic Process*, 4th Ed., Macmillan, 1977, Chapters 11 and 12, and the references cited therein. Useful classes of organic developing agents include hydroquinones, catechols, aminophenols, pyrazolidones, phenylenediamines, tetrahydroquinolines, bis(pyrazolidones)amines, cycloalkenones, pyrimidines, reductiones and coumarins. Useful inorganic developing agents include compounds of a metal having at least two distinct valence states, which compounds are capable of reducing ionic silver to metallic silver. Such metals include iron, titanium, vanadium and chromium, and the metal compounds employed are typically complexes with organic compounds such as polycarboxylic acids or aminopolycarboxylic acids. Included among useful developing agents are the iodohydroquinones of Duennbier et al U.S. Patent 3,297,445, the aminoalkoxy cycloalkenones of Gabrielsen et al U.S. Patent 3,690,872, the 5-hydroxy and 5-aminopyrimidines of Wyand et al U.S. Patent 3,672,891, the N-acyl derivatives of p-aminophenols of Porter et al U.K. Patent 1,045,303, the 3-pyrazolidones of Kendall U.S. Patent 2,289,367, Allen U.S. Patent 2,772,282, Ishikawa et al U.S. Patent 4,845,016 Stewart et al U.K. Patent 1,023,701 and DeMarle et al U.S. Patents 3,221,023 and 3,241,967, the anhydrihydro reductiones of Gabrielsen et al U.S. Patent 3,672,896, the heterocyclic-sulfonhydrazides of Clarke et al EPO 0 545 491, the N-(4-aminophenyl)pyrrolidine derivatives of Ohki et al U.S. Patent 5,278,034, the 6-aminotetrahydroquinolines of Taniguchi et al EPO 0 670 312, the heterocyclic compounds of Hagemann DE 4,241,532, and the 6-hydroxy and 6-aminocoumarins of Ofstedahl U.S. Patent 3,615,521. Particularly useful primary aromatic amino color developing agents are the p-phenylenediamines and especially the N-N-dialkyl-p-phenylenediamines in which the alkyl groups or the aromatic nucleus can be substituted or unsubstituted. Common p-phenylenediamine color developing agents are N-N-diethyl-p-phenylenediamine monohydrochloride, 4-N,N-diethyl-2-methylphenylenediamine monohydrochloride, 4-(N-ethyl-N-2-methanesulfonyl-aminoethyl)-2-methylphenylenediamine sesquisulfate monohydrate, and 4-(N-ethyl-N-2-hydroxyethyl)-2-methylphenylenediamine sulfate. Other p-phenylenediamines, similar compounds, and their use include those described in Nakamura et al U.S. Patent 5,427,897, Miyayashi et al U.S. Patent 5,380,625, Haijima et al U.S. Patent 5,328,812, Taniguchi et al U.S. Patent 5,264,331, Kuse et al U.S. Patent 5,202,229, Mikoshiba et al U.S. Patent 5,223,380, Nakamura et al U.S. Patent 5,176,987, Yoshizawa et al U.S. Patent 5,006,437, Nakamura U.S. Patent 5,102,778 and

volume in the processing channel is at least 40 percent of the total volume of processing solution in the system. In order to provide efficient flow of the processing solution through the opening or nozzles into the processing channel, it is desirable that the nozzles/opening that deliver the processing solution to the processing channel have a configuration in accordance with the following relationship:

$$F \leq P/A \leq 40$$

wherein:

F is the flow rate of the solution through the nozzle in gallons per minute and  
A is the cross sectional area of the nozzle provided in square inches.

Low volume thin tank systems are described in more detail in Bartell et al U.S. Patent 5,179,404, Rosenburgh et al U.S. Patent 5,270,762, Earle U.S. Patent 5,294,956, Earle et al WO 91/12567, Earle WO 91/19226, Glover et al WO 92/07301 and WO 92/07302, Glover WO 92/09332, Glover et al WO 92/10790, Earle WO 92/17370, Earle et al WO 92/17819, Glover et al WO 93/00612, Earle et al WO 93/04404, Paton et al EPO 0 559 025, Bartell et al EPO 0 559 026, Picquino et al EPO 0 559 027, Rosenburgh et al EPO 0 559 028, and Bartell et al EPO 0 559 029.

(9) The amount of effluent produced by the processing system may be reduced by reducing replenishment rates and reusing and regenerating previously used solutions. Replenishers may be one part or multipart and concentrated replenishers are preferred to reduce volume. If the materials that wash out of the light-sensitive material are found to increase to an objectionable concentration, the overflow solution can be treated to remove the objectionable material, for example with ion-exchange resins. Various methods of reducing effluent for color developers are described in Kaneko et al U.S. Patent 4,297,437, Ishikawa et al U.S. Patent 4,797,351, Marsden et al U.S. Patent 4,983,504, Wernicke et al U.S. Patent 4,997,749, Meckl et al U.S. Patent 5,004,676, Naruse et al U.S. Patent 5,024,924, Abe U.S. Patent 5,068,170, Yoshida et al U.S. Patent 5,077,180, Ishikawa et al U.S. Patent 5,147,766, Yamada U.S. Patent 5,178,994, Green et al U.S. Patent 5,279,930, Yoshida et al U.S. Patent 5,246,819, Yoshida et al U.S. Patent 5,391,467, Andoh et al EPO 0 325 277, Ontani et al EPO 0 350 046, Kanada et al EPO 0 450 554, Satake et al EPO 0 468 781, Hasebe EPO 0 538 875, Fyson et al WO 91/07699, Koshimizu et al U.S. Patent 4,820,623, Aida et al U.S. Patent 4,849,324, and Goto et al EPO 0 452 886.

(10) High silver bromide films are described to be rapidly processed using color developing solutions wherein the level of bromide ion, and the processing temperature, are controlled in Fujimoto et al U.S. Patent 5,344,750.

Nakagawa et al U.S. Patent 5,043,254. Advantageous results can be obtained with combinations of organic and inorganic developing agents as described in Vought Research Disclosure, Vol. 150, October, 1976, Item 15034, and with combinations of different types of organic developing agents such as the combination of anhydrosulfonamide reductions and aminomethyl hydroquinones of Youngquist U.S. Patent 3,666,457, the combination of a color developer and a 3-pyrazolidone of Twist WO 92/10789 and the combination of ascorbic acid and 3-pyrazolidone of Sutherns U.K. Patent 1,281,516. Developing agents can be incorporated in photographic elements in the form of precursors. Examples of such precursors include the halogenated acyl hydroquinones of Porter et al U.S. Patent 3,246,988, the N-acyl derivatives of aminophenols of Porter et al U.S. Patent 3,291,609, the reaction products of a catechol or hydroquinone with a metal described in Barr U.S. Patent 3,295,978, the quinhydrone dyes of Haefner et al U.S. Patent 3,565,627, the cyclohex-2-ene-1,4-diones and cyclohex-2-ene-1-one-4-monoketals of Chapman et al U.S. Patent 3,586,506, the Schiff bases of *p*-phenylenediamines of Pupo et al Research Disclosure, Vol. 151, November, 1976, Item 15159 and the blocked developers of Southby et al U.S. Patent 5,256,525. Precursors may also be contained in developing solutions as described in Mikoshiba et al EPO 0 393 523 and Yagihara et al U.S. Patent 5,002,862. When incorporated, the developing agents can be present in one or more hydrophilic colloid layers of the photographic element, such as a silver halide emulsion layer or a layer adjacent the silver halide layer, as illustrated by Haefner U.S. Defensive Publication T-882020. The developing agent can be added to the layer in the form of a dispersion with a film-forming polymer in a water-immiscible solvent as illustrated by Dunn et al U.S. Patent 3,518,088, as a dispersion with a polymer latex as illustrated by Chen Research Disclosure, Vol. 159, July, 1977, Item 15930, and Pupo et al Research Disclosure, Vol. 148, August, 1976, Item 14850, or as a solid particle dispersion as described by Texter et al U.S. Patent 5,240,821. Incorporated primary amine color developing agents or precursors therefore are also used in photographic elements that are processed in low volumes of processing solutions as described by Texter et al U.S. Patent 5,411,840.

Incorporated ballasted heterocyclicsulfonhydrazide color developing agents can be included in color photographic elements to produce color images in response to alkaline solutions, as described by Clarke et al U.S. Patent 5,284,739.

#### B. Preservatives

The color developer normally contains a preservative to protect the color developer from decomposition. Preservatives include sulfites, such as sodium sulfite, potassium sulfite, sodium bisulfite, potassium bisulfite, sodium metabisulfite, potassium metabisulfite, and carbonyl sulfite adducts, hydroxylamine and hydroxylamine derivatives, hydroxamic acids, hydrazines

and hydrazides, phenols, hydroxyketones, aminoketones, mono- and polysaccharides, monoamines, diamines, polyamines, quaternary ammonium salts, nitroxy radicals, alcohols, oximes, diamide compounds, and condensed ring-type amines. Preservatives for use with high chloride films are described in Vincent et al U.S. Patent 4,892,804. Examples of various preservatives are the hydrazines of Onki et al U.S. Patent 4,801,521, Ishikawa et al U.S. Patent 4,960,684, Andoh et al EPO 0 325 276 and EPO 0 325 277, and Miyazaki et al EPO 0 326 061, monosaccharides of Satake EPO 0 597 179, the hydroxyketones of Hässler et al German OLS 3,801,536 and U.K. Patent Application 2,214,322, the hydroxylamine derivatives of Morimoto et al U.S. Patent 4,800,153, Ishikawa et al U.S. Patent 4,801,516, Ohki et al U.S. Patent 4,833,068, Kobayashi et al U.S. Patent 4,837,139, Ishikawa et al U.S. Patent 4,876,174, Ishikawa et al U.S. Patent 4,965,176, Yoneyama et al U.S. Patent 5,004,675, Yoshida et al U.S. Patent 5,066,571, Morimoto U.S. Patent 5,094,937, Fujimoto U.S. Patent 5,100,765, Yoshida et al U.S. Patent 5,178,992, Kobayashi et al U.S. Patent 5,354,646, Marrese et al U.S. Patent 5,508,155, Kobayashi et al EPO 0 269 740, Nagaoka et al EPO 0 315,952, and Satake EPO 597 179, the amines of Ishikawa et al U.S. Patent 4,798,783 and Andoh et al U.S. Patent 4,897,339, the aromatic sulfonic acids of Nakamura et al U.S. Patent 5,204,229, the polyol compounds of Loiacono et al EPO 0 459-103, the amino acids of Buongiorno et al EPO 0 530 921, the compounds discussed in Yoshida et al U.S. Patent 5,077,180 in Sigemori et al EPO 0 636 937, and the poly(N-hydroxyl alkyleneamines) of Sigemori et al EPO 0 621 507.

#### C. Antifoggants

An antifoggant may be used in a developing solution if required. Antifoggants that can be added include alkali metal halides, such as sodium or potassium chloride, sodium or potassium bromide, sodium or potassium iodide, and organic antifoggants, particularly nitrogen-containing heterocyclic compounds such as benzotriazole, 6-nitrobenzimidazole, 4-nitrobenzotriazole, 5-nitrobenzotriazole, 5-chloro-benzotriazole, 5-nitroisobenzimidazole, 2-thiazolyl-methylbenzimidazole, indazoles, hydroxyazindoline, and adenine. The use in developing solutions of other nitrogen-containing heterocyclics and mercapto nitrogen-containing compounds is described in Morimoto et al U.S. Patent 4,851,325, Yoshida et al U.S. Patent 5,110,713, Ishikawa et al U.S. Patent 4,863,836, Momoki et al U.S. Patent 4,853,321 and Murai et al U.S. Patent 4,963,475. The use of sulfur-containing ring compounds is described in Yagihara et al U.S. Patent 4,842,993.

#### D. Sequestering agents

Various sequestering agents may be added to the color developer to prevent precipitation of calcium and magnesium or



for improving the stability of the color developer. Particularly useful chelating agents are the organic acids, such as aminopolycarboxylic acids, organic phosphonic acids, and phosphonocarboxylic acids, examples of which are nitrilotriacetic acid, diethylenetriaminediacetic acid, ethylenediaminetetraacetic acid, N,N',N'-trimethylene phosphonic acid, ethylenediaminetetraacetic acid, N,N',N'-tetramethylene phosphonic acid, cyclohexanediaminetetraacetic acid, 1,2-diaminopropanetetraacetic acid, hydroxyethylenediaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediamine ortho-hydroxyphenylacetic acid, 2-phosphonobutane-1,2,4-tricarboxylic acid, 1-hydroxyethylidene-1,1-diphosphonic acid, N,N'-bis(2-hydroxybenzyl)ethylenediamine-N,N'-diacetic acid, triethylenetetraaminehexaacetic acid, 1,3-diamino-2-propanol tetraacetic acid, nitrilotripropionic acid, hydroxyethylenediaminetetraacetic acid, catechol-3,4,6-trisulfonic acid, catechol-3,5-disulfonic acid, 5-sulfosalicylic acid, 4-sulfosalicylic acid, 6-aminodiacetic acid, and glycinedipropionic acid. Hydroxyalkylidene diphosphonic acid chelating agents can effectively sequester both iron and calcium and may be utilized in combination with small amounts of lithium salts as described in Brown U.S. Patent 3,839,045. Chelating agents may be used in combination, such as the combination of a polyhydroxy compound and an aminocarboxylic acid of Buongiorno et al U.S. Patent 4,975,357. The use of various chelating agents in a developer is described in Ishikawa et al U.S. Patent 4,835,092, Ishikawa et al U.S. Patent 4,906,554, Fujimoto et al U.S. Patent 4,837,132, Marchesano et al U.S. Patent 4,873,180, Fujita et al U.S. Patent 4,853,318, Shiba et al U.S. Patent 5,053,322, Kuze Japanese Kokai JP 4,062,545 and Takabayashi et al EPO 0 528 406.

#### E. Other additives

Buffering agents may be used to maintain the pH of the developer. These may include sodium carbonate, potassium carbonate, sodium bicarbonate, potassium bicarbonate, trisodium phosphate, tripotassium phosphate, disodium phosphate, dipotassium phosphate, sodium borate, potassium borate, sodium tetraborate (borax), and potassium tetraborate, sodium o-hydroxybenzoate (sodium salicylate), potassium o-hydroxybenzoate, sodium 5-sulfo-2-hydroxybenzoate (sodium 5-sulfosalicylate), and potassium 5-sulfo-2-hydroxybenzoate (potassium 5-sulfosalicylate), as well as other alkali metal carbonates, borates or phosphates. Water-soluble sulfonated polystyrene may be used to improve the clarity of the developer solution and reduce the tendency for tarring to take place. The developer may contain stain-reducing agents such as triazynyl stilbenes and the compounds of Fujimoto et al EPO 0 488 217 and anti-bacterial or anti-fungal agents, such as described in Yoshida et al EPO 0 330 093. The developer may contain compounds to increase the solubility of the developing agent, such as methyl cellosolve, methanol, acetone, dimethyl formamide, cyclodextrin, dimethyl formamide, diethylene glycol, ethylene glycol, and the solubilizing agents described in

Loiacono et al U.S. Patent 5,273,865, Satake EPO 0 556 716 and Yoshimoto et al EPO 0 500 370. Water-insoluble photographic adjuvants (such as sensitizing dyes) can be mixed with cyclodextrins to form water soluble adducts for use in developers, as described by Fodor et al EPO 0 568 850. Nonionic surfactants and anionic, cationic, or amphoteric surfactants such as described in Ueda et al EPO 0 436 947 may be added to the developer. If necessary, various other components may be added to the color developer solution such as dye-forming couplers, competitive couplers, halides, fogging agents such as sodium borohydride, anti-sludging compounds such as described in Morimoto EPO 0 507 284 and the compounds of Yoshimoto et al EPO 0 514 906. Silver may be removed as described by McGuckin et al U.S. Patent 5,210,009 and 5,188,662. Water-soluble silicone compounds can be used in color developers as described in Ishikawa et al EPO 0 573 002. Thiourea compounds may be included in the color developers as described in Ishikawa et al EPO 0 573 956. Anti-sludging agents may also be included in the processed elements to allow for lower developer replenishment rates as described in EPO 0 676 667.

#### XX. Desilvering, washing, rinsing and stabilizing

The desilvering stage comprises a bleaching step to change the developed silver back to an ionic-silver state and a fixing step to remove the ionic silver from the light-sensitive material. These two processes may be combined into a monobath bleach-fix. If necessary, additional processing steps may be added, such as a washing step, a stopping step, a stabilizing step and a pretreatment step to accelerate bleaching, fixing or bleach-fixing. Where a silver image is desired, bleaching is omitted.

##### A. Bleaching

(1) Bleaching agents which may be used include compounds of polyvalent metal such as iron (III), cobalt (III), chromium (VI), and copper (II), peracids, quinones, and nitro compounds. Typical bleaching agents are iron (III) salts, such as ferric chloride, ferricyanides, bichromates, and organic complexes of iron (III) and cobalt (III). Ferric complexes of aminopolycarboxylic acids and persulfate are most commonly used. Those bleaching agents having a redox potential of at least 150 mV, preferably at least 200 mV, as measured by the method described in *Transactions of the Faraday Society*, Volume 55, 1312-1313 (1959), may be used for quicker bleaching. Examples of useful ferric complexes include complexes of nitrilotriacetic acid, ethylenediaminetetraacetic acid, 1,3-propylenediaminetetraacetic acid, 1,2-propylenediaminetetraacetic acid, diethylenetriamine pentaacetic acid, ethylene glycol bis(aminooethyl ether)tetraacetic acid, diaminopropanol tetraacetic acid, N-(2-hydroxyethyl)ethylenediaminetetraacetic acid, ethylenediaminodipropionic acid, methyliminodiacetic acid, ethylenediaminodiacetic acid, and the solubilizing agents described in

acetic acid, cyclohexanediaminetetraacetic acid, glycol ether diaminetetraacetic acid, ethylenediamine-N-( $\beta$ -oxyethyl)-N,N'-triacetic acid, 1,4-diaminobutanetetraacetic acid, iminodiacetic acid, ethylenediaminetetrapropionic acid, (2-acetamido)iminodiacetic acid, dihydroxyethylglycine, ethylenediamine-di-o-hydroxyphenylacetic acid, nitrilotriacetate, ethylenediamine-glycinedipropionic acid, ethylenediaminedisuccinic acid, N,N-dicarboxyanthranilic acid, and b-alaninediacetic acid. Also useful are ternary ferric-complex salts formed by two different ligands, such as those described in Buchanan et al U.S. Patent 5,521,056, or a tetradentate ligand and a tridentate ligand. Additional ligands and their use are described in Ueda et al U.S. Patents 4,804,618 and 4,894,320, Haruuchi et al U.S. Patent 4,910,125, Fujimoto et al U.S. Patent 4,985,347, Nakazyo et al U.S. Patent 5,002,861, Kunitz et al U.S. Patent 5,009,985, Foster et al U.S. Patent 5,061,608, Nakamura U.S. Patent 5,093,228, Okada et al U.S. Patent 5,188,927, Yoshimoto et al U.S. Patent 5,204,228, Okada et al U.S. Patents 5,217,855 and 5,223,379, Tappe et al U.S. Patent 5,238,791, Abe et al U.S. Patent 5,246,821, Okada et al U.S. Patents 5,250,401, 5,250,402, 5,254,444, 5,256,531 and 5,300,408, Foster et al U.S. Patent 5,334,491, Inaba et al U.S. Patent 5,338,649, Abe et al U.S. Patent 5,350,668, Okada et al U.S. Patent 5,352,567, Ueda et al U.S. Patent 5,391,466, Szajewski et al U.S. Patent 5,443,943, Hagiwara et al EPO 0 293 729, Ishikawa et al EPO 0 450 293, Inaba et al EPO 0 530 828, Ueda et al EPO 0 532 003, Foster et al EPO 0 545 464, Ueda et al EPO 0 553 569, Yamashita et al EPO 0 556 782, Ueda et al EPO 0 563 571, Seki et al EPO 0 567 126, Kuwae et al EPO 0 584 665, Fujita et al EPO 0 595 102, Inaba et al EPO 0 649 057, Suzuki et al EPO 0 654 705, Okada et al EPO 0 657 777, Wichmann et al German OLS 3,939,756, Tappe et al German OLS 4,029,805 and Tappe et al German OLS 4,226,372. These ferric aminopolycarboxylate complexes are used in the form of salts, for example, as sodium, potassium, lithium, cesium or ammonium salts. Ferric chelates formed from polyamino disuccinic acids are described in Wilson et al WO 94/28464.

(2) Typical peracid bleaches include the hydrogen, alkali and alkali earth salts of persulfate, peroxide, perborate, perphosphate, and percarbonate, and the related perhalogen bleaches such as hydrogen, alkali and alkali earth salts of chlorate, bromate, iodate, perchlorate, perbromate and metaperiodate. Particularly useful peracid bleaches are sodium persulfate and hydrogen peroxide. Examples of formulations using these agents are described in Research Disclosure, December 1989, Item 308119, Research Disclosure, May, 1977, Item 15704; Research Disclosure, August, 1981, Item 20831; DE 3,919,551, Eastman Kodak Publication H-24, Manual for Processing Eastman Color Print Films (December, 1988) and the Journal of the Society of Motion Picture and Television Engineers (SMPTe), Vol. 91, pp. 158-163 (1982); SMPTe, Vol. 91, pp. 1058-1065, SMPTe, Vol. 95, pp. 220-223. Additional

hydrogen peroxide and persulfate formulations are described in Koboshi et al U.S. Patent 4,277,556, Idota et al U.S. Patents 4,301,236 and 4,328,306, Brien et al U.S. Patent 4,454,224, Hall et al U.S. Patents 4,717,649 and 4,737,450, English et al U.S. Patent 5,318,880, Buchanan et al U.S. Patent 5,521,056, Nakamura EPO 0 428 101, Marsden et al WO 92/01972, Fyson et al WO 92/07300, Fyson WO 93/11459, Häsel et al German OLS 3,919,551 and Japanese Patent Applications JP 61/250647 and JP 61/261739.

(3) Various compounds may be used to catalyze or accelerate bleaching. These may be divided into classes of compounds which accelerate specific bleach types such as those which accelerate peracid bleaches or those which accelerate iron chelate bleaches, and those which accelerate bleaching in general. Bleaching accelerators can be added to the bleaching bath and the prebaths thereof. Examples of bleaching accelerators are described in Mourey et al U.S. Patent 3,706,561, VanDerVoorn et al U.S. Patent 3,707,374, Smith U.S. Patent 3,772,020, Shirasu et al U.S. Patent 3,820,997, Shimamura et al U.S. Patent 3,870,520, Wabnitz, Jr. U.S. Patent 3,893,858, Kishimoto et al U.S. Patent 4,446,225, Yamamuro et al U.S. Patent 4,458,010, Nakajima et al U.S. Patent 4,506,007, Yamamuro et al U.S. Patent 4,508,816, Ohno et al U.S. Patents 4,508,817 and 4,578,345, Lau et al U.S. Patent 4,552,834, Harder et al U.S. Patent 4,865,956, Ueda et al U.S. Patent 4,914,009, Harder et al U.S. Patent 4,923,784, Bergthaller et al U.S. Patent 4,939,075, Morimoto et al U.S. Patent 5,011,763, Sakanoue U.S. Patent 5,114,835, Buchanan et al U.S. Patent 5,460,924, O'Toole et al U.S. Patent 5,508,151, O'Toole U.S. Patent 5,510,232, Ueda et al EPO 0 287 073, Bergthaller et al EPO 0 299 296, Buchanan et al EPO 0 602 600, Nagaoka et al EPO 0 407 206, Meckl et al U.K. Patent 1,138,842, Keiler et al East German DD 141,727, Pollet et al German OLS 2,748,430, Pollakowski et al German OLS 3,234,467, Bergthaller et al German OLS 3,613,793, Häsel et al German OLS 3,919,550, Feil et al German Patent 3,919,551, Goto et al Japanese Patent Application 1/292339, Price et al Research Disclosure, Vol. 157, May, 1977, Item 15704, and Sels et al Research Disclosure, Vol. 208, August, 1981, Item 20821.

(4) Additional chelating agents may be present in the bleach solution. These may be, for example, aminopolycarboxylic, phosphonic acids, and hydroxy-substituted agents as described by Stephen et al U.S. Patent 4,933,266. Water-soluble aliphatic carboxylic acids such as acetic acid, citric acid, propionic acid, hydroxyacetic acid, butyric acid, malonic acid, and succinic acid may be utilized to combat the undesirable increase in Dmin which results from bleach induced dye formation as described in U.S. Patent 5,061,608. Other organic acids may be used as described in Hagiwara et al EPO 0 243 866. When starting bleach tanks are prepared, a solution commonly known in the photographic industry as a "bleach starter" is added to the bleach replenisher solution. Bleach starters include ammonia,

ammonium hydroxide, potassium hydroxide, potassium carbonate, sodium hydroxide, aqueous ammonia, diethanolamine, monoethanolamine, imidazole, or primary or secondary amine having a hydroxyalkyl group as an alkaline agent, sodium acetate, potassium acetate and ammonium acetate as described in Foster EPO 0 664 481. The bleaching solution can contain rehalogenating agents such as bromides and chlorides. Potassium, sodium, or ammonium nitrate is used as an anti-corrosion agent to protect metal. In order to adjust the pH, buffering agents such as acetic acid, glycolic acid or malonic acid can be added in conjunction with an alkaline agent such as aqueous ammonia. In addition, mineral acids such as hydrochloric acid, nitric acid, sulfuric acid and phosphoric acid can normally be used for the acid component and these acids can be used as a mixture with one or more salt of the weak acids previously mentioned above in order to provide a buffering effect. Other buffers are described in Foster et al U.S. Patent 5,061,608, Okada et al U.S. Patents 5,250,401 and 5,250,402, Kuse et al U.S. Patent 5,236,814, Okada et al EPO 0 461,413, Kuse et al EPO 0 475 768, Kuse EPO 0 534 086, Ueda et al EPO 0 553 569, and Kamata et al EPO 0 556 782. Bleaching solutions or pre-bleaches may contain other addenda such as sulfites, non-chelated salts of aminopolycarboxylic acids, scum-reducing agents as described in Schwartz U.S. Patent 4,839,262, dye-stabilizers as described in Cullinan et al U.S. Patents 4,960,682, 4,921,779, and 4,975,356 and Daecke et al German OLS 4,226,651, anti-calcium agents, and/or anti-phosphate agents, antifogants, brighteners, and compounds to capture developer as described in Tappe et al 0 498 950. Persulfate bleaches may contain chlorine scavengers, as described in Research Disclosure, (1978) Item 17556 and Itoh et al U.S. Patents 4,292,401 and 4,293,639.

#### B. Fixing

(1) Fixing agents are water-soluble solvents for silver halide such as a thiosulfate (e.g., sodium thiosulfate, ammonium thiosulfate, and potassium thiosulfate), a thiocyanate (e.g., sodium thiocyanate, potassium thiocyanate and ammonium thiocyanate), a thioether compound (e.g., ethylenedithioglycolic acid and 3,6-dithia-1,8-octanediol), a thioglycolic acid or a thiourea, an organic thiol, an organic phosphine, a high concentration of halide, such as bromide or iodide, a mesoionic thiolate compound, and sulfite. These fixing agents can be used singly or in combination. Thiosulfate is preferably used and ammonium thiosulfate, in particular, is used most commonly owing to the high solubility. Alternative counter-ions such as potassium, sodium, lithium, cesium as well as mixtures of two or more cations may be used. Some fixing agents and their use in solid and liquid formulations are described in Mader U.S. Patent 2,748,000, Bard U.S. Patent 3,615,507, Nittel et al U.S. Patent 3,712,818, Smith U.S. Patent 3,722,020, Ling U.S. Patent 3,959,362, Greenwald U.S. Patents 4,126,459, 4,211,562, and

4,211,559, Atland et al U.S. Patent 4,378,424, Fyson U.S. Patents 5,171,658, 5,244,778 and 5,275,923, Rogers et al U.S. Patent 5,389,501, Kojima et al EPO 0 458 277, EPO 0 431 568, and EPO 0 500 045, Hayashi EPO 0 557 851, Buttner et al EPO 0 610 763, and Kojima et al EPO 0 611 990. Some low ammonia fixing solutions are described in Schmittou et al U.S. Patent 5,183,727, Yoshimoto et al EPO 0 466 510, Fyson EPO 0 550 933 and Srajewski et al EPO 0 605 036, EPO 0 605 038 and EPO 0 605 039.

(2) The fixing or bleach-fixing solution may also contain preservatives such as sulfites (e.g., sodium sulfite, potassium sulfite, and ammonium sulfite), bisulfites (e.g., ammonium bisulfite, sodium bisulfite, and potassium bisulfite), metabisulfites (e.g., potassium metabisulfite, sodium metabisulfite, and ammonium metabisulfite), hydroxylamines, hydrazines, bisulfite adducts of carbonyl and aldehyde compounds (e.g., acetaldehyde sodium bisulfite), ascorbic acid, mercapto-substituted N-oxide compounds, and sulfonic acid compounds, e.g., as described in Watanabe et al U.S. Patent 5,288,595. Compounds which may be added to accelerate fixing include polyoxyethylene compounds, amine salts or amidine thiosulfates, ammonium or amine salts and organic amines, ammonium thiocyanate (ammonium rhodanide), thiourea and thioethers (for example, 3,6-dithia-1,8-octanediol) in combination with thiosulfates. Some fixing accelerators and their use are described in U.K. Patent 1,306,315, Barnes U.S. Patent 2,174,494, Photographische Industrie, 40, 249 (1942), Schmittou et al U.S. Patent 5,424,176 and EPO 0 569 008, and Rogers et al EPO 0 578 309. Sulfite fix accelerators are described in Fyson EPO 0 411 760.

(3) In order to adjust the pH of the fixing solution an acid or a base may be added, such as hydrochloric acid, sulfuric acid, nitric acid, acetic acid, bicarbonate, ammonia, potassium hydroxide, sodium hydroxide, sodium carbonate or potassium carbonate. The fixing solution may contain sequestering agents such as aminopolycarboxylic and phosphonic acids. Some sequesterants and their use are described in Fujita et al U.S. Patent 4,963,474, Craver et al U.S. Patent 5,343,035 and P.S. Patent 5,508,150, and Tappe et al EPO 0 486 909. Fixing solutions may also contain polymers as described in Fushiki et al U.S. 4,138,257 and Kojima et al U.S. Patent 4,948,711, solubilizing agents as described in Ikegawa et al U.S. Patent 5,097,042, stain reducing agents as described in Sasaki et al U.S. Patent 5,120,635, and surfactants as described in Ueda et al EPO 0 441 309.

(4) Some variations on the fixing processes already described include the high agitation process of Fujita et al U.S. Patent 5,221,597, the fixing solution reuse of Tsuchiya et al EPO 0 465 076, the fixing cover sheet of Simons WO 93/12462, the processes of Ueda et al U.S. Patent 5,194,368 and Nagashima et al U.S. Patent 5,066,569, and the solid formulations of Kim et al U.S. Patent 5,270,154.

### C. Bleach-fixing

The bleaching and fixing steps can be combined into a monobath bleach-fix step that can be used alone or in combination with the bleaching and the fixing step. A monobath bleach-fix is often used with a color paper process, such as the RA-4 Process described in the *British Journal of Photography Annual*, 1988, pp. 198-199. Examples of bleach-fixing solutions or dry formulations, and their use are further described in Hall et al U.S. Patent 4,717,649, Ueda et al U.S. Patent 4,818,673, Abe et al U.S. Patent 4,857,441, Häselser et al U.S. Patent 4,933,264, Ishikawa et al U.S. Patent 4,966,834, Spriewald et al U.S. Patent 4,987,038, Long et al U.S. Patent 5,055,382, Abe et al U.S. Patent 5,104,775, Goto et al U.S. Patent 5,147,765, Tappe et al U.S. Patent 5,149,618, Ishikawa U.S. Patent 5,169,743, Kobayashi et al U.S. Patent 5,180,656, Yoshida et al U.S. Patent 5,310,633, Fyson U.S. Patent 5,354,647, Ishikawa et al U.S. Patent 5,434,097, Goto et al U.S. Patent 5,479,262, Nakamura et al U.S. Patent 5,565,023, Yoshida et al U.S. Patent 5,569,852, Gordon et al U.S. Patent 5,590,583 (bleach-fix replenisher) and EPO 0 645 674, Kamada et al U.S. Patent 5,586 875, and Wernicke et al German OLS 4,000,482.

### D. Washing, rinsing and stabilizing

(1) After the completion of development and desilvering, there are often additional steps of washing, rinsing or stabilizing which serve to stabilize the photographic elements. These processing solutions can contain various kinds of surface active agents for preventing the occurrence of water drop unevenness when the color photographic materials are dried. The surface active agents may include alkylphenolethylene oxide addition products such as alkylphenol, octylphenol, nonylphenol, dodecylphenol and dinonylphenol, polyethylene glycol type nonionic surface active agents, polyhydric alcohol type nonionic surface active agents, alkylbenzenesulfonate type anionic surface active agents, higher alcohol sulfonic acid ester type anionic surface active agents, alkylphthalenesulfonate type anionic surface active agents, amine salt type cationic surface active agents, quaternary ammonium salt type cationic surface active agents, amino acid type amphoteric surface active agents and silicone series surface active agents having a high defoaming effect. Precipitate and scum-reducing agents may be added such as sorbitan esters of fatty acids substituted with ethylene oxide, polyoxyethylene compounds described in Hazenbosch et al U.S. Patent 4,059,446, and *Research Disclosure*, vol 191, 19104 (1980), and polymers or copolymers having a pyrrolidone nucleus unit, such as poly-N-vinyl-2-pyrrolidone. Other agents which may be added include chelating agents such as aminopolycarboxylic acids and phosphoric acids, organic solubilizing agents, such as ethylene glycol, stain-reducing agents, optical whitening agents, acids or bases to adjust the pH, and buffers to maintain the pH. These processing solutions may also contain various anti-bacterial agents or antifungal agents such as thiazolylbenzimidazoles,

isothiazolones, for example, 5-chloro-2-methyl-4-isothiazolin-3-one, 2-methyl-4-isothiazolin-3-one and 2-octyl-4-isothiazolin-3-one, chlorophenols such as trichlorophenol, bromophenols, organotin or organozinc compounds, thiocyanic or isothiocyanic acid compounds, acid amides, diazines or triazines, thioureas, benzotriazolealkylguanidines, quaternary ammonium salts such as benzammonium chloride, antibiotics such as penicillin and the antifungal agents described in *Journal of Antibacterial and Antifungal Agents*, Vol. 11, No. 5, 207-223 (1983) and Deegan, J. *Imaging Tech.*, Vol. 10, pp. 26-28, 1984. Some representative rinses and washes are described in Meckl et al U.S. Patent 4,855,216, Kuse et al U.S. Patent 4,980,272, Morigaki et al U.S. Patent 5,006,456, Abe et al U.S. Patent 5,034,308 and 5,077,179, Kuse et al U.S. Patent 5,206,119, Takemura et al U.S. Patent 5,415,979, Ueda et al U.S. Patent 5,465,228, McGuckin et al U.S. Patent 5,485, and Carli et al WO 91/05289.

(2) A stabilization solution used to stabilize dye images also contains a dye stabilizing agent such as formaldehyde or formaldehyde precursors, such as N-methylol-pyrazole, hexamethylenetetramine, formaldehyde-bisulfite adduct, and dimethylol urea. A stabilizing solution may also contain, if necessary, ammonium compounds such as ammonium chloride and ammonium sulfite, compounds of a metal such as Bi, Mg, Zn, Ni, Sn, Ti, Zr and Al, N-methylol compounds, various kinds of stabilizers, hardening agents, and alkanolamine compounds. Various stabilizer formulations and their use are shown in Mackey U.S. Patents 2,487,569 and 2,579,435, Ishikawa et al U.S. Patent 4,778,743, Schwartz U.S. Patent 4,786,583, Gornel U.S. Patent 4,859,574, Schwartz U.S. Patents 4,923,782 and 4,927,746, Cullinan et al U.S. Patent 5,037,725, Kuse et al U.S. Patent 5,110,716, Hagiwara et al U.S. Patent 5,188,925, Morigaki et al U.S. Patent 5,217,852, Fujita et al U.S. Patent 5,334,493, Kawamura et al U.S. Patent 5,360,700, Ishikawa et al U.S. Patent 5,474,461, Tsuchiya et al U.S. Patent 5,476,434, Morigaki et al U.S. Patent 5,504,609, Hagiwara et al U.S. Patent 5,506,349, Morigaki et al U.S. Patent 5,519,190, Kobayashi et al U.S. Patent 5,521,477 and EPO 0 529 794, Kona et al U.S. Patent 5,530,832, Kuwae et al U.S. Patent 5,534,608, Hagiwara et al U.S. Patent 5,551,757, Darmon et al U.S. Patent 5,577,041, and McGuckin et al WO 93/23793.

(3) In order to reduce the amount of wash water or stabilizer solution used in the wash step or the stabilization step, a multistage countercurrent system is used and the number of stages is preferably from 2 to 4. A multistage countercurrent system is described in *Journal of the Society of Motion Picture and Television Engineering*, Vol. 64, 248-253 (May 1955). To further minimize the volume of water used, the used wash water can be recovered and treated to remove chemical constituents that have washed out of the light-sensitive photographic material or that have been carried over from a previous solution by the light sensitive material. Common treatment procedures include use of ion-exchange resins, precipitation and filtration of components,

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and distillation. Replenishment rates are kept as low as possible, and many of the additives described above are used to allow for reduced rates. Additional methods for reducing effluent are described in Ueda et al U.S. Patent 4,804,616, Fujita et al U.S. Patent 4,855,218, Kishimoto et al U.S. Patent 5,001,041, Abe U.S. Patent 5,009,983, Abe U.S. Patent 5,108,879, Ishikawa et al U.S. Patent 5,139,929, Wernicke et al U.S. Patent 5,210,008, Wernicke et al EPO 0 501 229, and Abe EPO 0 409 065.

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